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SECONDARY ZINC INDUSTRY EMISSION CONTROL PROBLEM DEFINITION STUDY

PART 1—TECHNICAL STUDY

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ERRATA FOR SECONDARY ZINC INDUSTRY EMISSION CONTROL PROBLEM DEFINITION STUDY, PART 1 - TECHNICAL STUDY FINAL REPORT

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Page (V-4) - At the bottom of this page, begin new paragraph by inserting the following line:

"Findings of this study indicate that there are significant carbonaceous"

Table VII-1 (Page 1 of 2) - In Column 7, the fourth item from the top, delete the decimal point that precedes the number "32".

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Effluents containing particulate and gaseous emissions are exhausted from certain processes of the secondary zinc industry. Data on those emissions with related emission-control and process data were obtained from a sampling of plants. These data were evaluated to obtain the results of this study. Emissions from sweat processes occur at very low rates where the processed zinc scrap contains only small amounts of impurities. However, very significant emissions of particulate and gaseous carbonaceous substances, and particulate zinc oxide and zinc chloride may occur when there are substantial amounts of impurities in the scrap. The results of this study indicate that emission factors for zinc sweat processes range from zero to around 32 pounds of particulate per ton of scrap material processed. The results further indicate that the emitted particulate may be composed of zero to 34 percent $ZnCl_2$; 40 to 100 percent ZnO; and small percentages of carbonaceous substance. Several emission-control concepts were developed based on findings of this study, and recommendations are made for further research and development. ( )

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SECONDARY ZINC INDUSTRY
EMISSION CONTROL PROBLEM DEFINITION STUDY

PART 1 - TECHNICAL STUDY

Conducted by the
AIR POLLUTION CONTROL OFFICE, EPA

in cooperation with

THE NATIONAL ASSOCIATION OF
SECONDARY MATERIAL INDUSTRIES

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Secondary Zinc Industry
Emission Control Problem Definition Study

Part 1 - Technical Study

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Secondary Zinc Industry

Emission Control Problem Definition Study

Part 1 - Technical Study

Abstract

Effluents containing particulate and gaseous emissions are exhausted from certain processes of the secondary zinc industry. Data on those emissions with related emission-control and process data were obtained from a sampling of plants. These data were evaluated to obtain the results of this study.

Process materials consumed by this industry consist principally of scrapped items that contain metallic zinc. Small amounts of chloride fluxing compounds are also consumed in some secondary zinc processes. The principal processes of the industry are sweating and distillation which are applied to recovery metallic zinc.

Sweat processing is conducted to produce finished zinc alloys; it is also a usual preliminary step to distillation, providing the crude zinc-alloy feed for the latter. Distillation processes produce zinc metal and zinc oxide, both of virtually 100% purity.

Emissions from sweat processes occur at very low rates where the processed zinc scrap contains only small amounts of impurities. However, very significant emissions of particulate and gaseous carbonaceous substances, and particulate zinc oxide and zinc chloride may occur where there are substantial amounts of impurities in the scrap. Smaller amounts of other metal oxides, metal chlorides, and ammonium chloride may also be emitted under this condition.

Emissions from distillation processes contain zinc oxide as the principal constituent. These emissions occur at significant rates, but are satisfactorily controlled using baghouses.

The results of this study indicate that emission factors for zinc sweat processes range from zero to around 32 pounds of particulate per ton of scrap material processed. The results further indicate that the emitted particulate may be composed of zero to 34% $ZnCl_2$; 40 to 100% ZnO; and small percentages of carbonaceous substance (in one instance 10%). These values do not take into account the sweat processing of scrap containing large amounts of organic material (e.g., assemblies that contain gaskets, lubricants, etc.), where carbonaceous emissions might preponderate. Such scrap is usually subjected to preliminary sweat processing, using afterburners in some instances, that satisfactorily incinerate the organic material and resulting carbonaceous emissions.

Sweat-process emissions are alleviated by selection of processes that appear optimum for the type of scrap being processed and by application of established types of gas cleaning equipment. High collection efficiencies have been obtained in such equipment applications. However, emission control problems have not been solved for processing all types of zinc scrap material. Limitations are imposed on endurance and effectiveness of gas cleaning devices, used in this way, by the following occurrences:

a. Corrosion of metallic fabricating materials and organic bag filter materials caused by emitted chlorides.
b. Blinding of dry fabric filters by adhering carbonaceous particles and deliquescent $ZnCl_2$.
c. Blinding of irrigated fabric filters by adhering carbonaceous particles.
d. Abrasive wear of fibrous glass bag-filter material during cleaning.

e. Limited temperature resistance of organic-fabric-filter materials.

f. Tar-like deposits and ignition hazards associated with carbonaceous emissions.

Process model units were formulated for study of present and conceptual emission control systems.

Several emission-control concepts were developed based on findings of this study, and recommendations are made for further research and development.

CHAPTER I

Introduction

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Chapter I

Introduction

PROBLEM AREA - PROCESSES STUDIED

Gaseous exhaust effluents containing deliquescent and corrosive metal chlorides are emitted from certain processes of the secondary zinc and aluminum industries. The study reported here was conducted to define the problems of controlling emissions, so characterized, that result specifically from secondary-zinc processes.

As dealt with here, the secondary zinc industry consists of those plants that process discarded and scrapped items and materials that contain metallic zinc for the primary purpose of recovering that metal. The principal processes employed are sweating and distillation. This study does not include reduction processes applied to obtain metallic zinc from zinc oxide contained in waste materials. In present practice, most materials of that type are processed through primary smelting establishments. Also excluded from this study is the processing of zinc-process wastes, which are principally of a chemical nature, to produce chemical products - that processing usually being done in plants of the chemical and other non-metallurgical industries. (Study of processes excluded here might be taken up in "Reduction in Belgian Retorts" APEM, pp. 294-6; and "Sal Skimmings" and "Chemical Residues" Mathewson, pp. 319-21.)

SCOPE OF STUDY

The problem definition study is intended to determine a basis for research and development to improve emission control capabilities of the industry studied.

The results of the study may also be used as a source of data for additional purposes brought about by legislation, including an annual report to Congress and the setting of emission control standards required under the Clean Air Act with Amendments of 1970.

Part 1, reported here, covers the technical phase of a study to define the problems of controlling emissions of the secondary zinc industry. Part 2 of this study is planned to cover the economic phase - to show the degree of emission control that can be attained for specific process situations, the cost of attaining that control, and situations where satisfactory control cannot be attained because of cost.

APPROACH TO STUDY

The approach in conducting this study was to hold discussions between APCO and NASMI representatives; review available literature; and visit a small sampling of plants that were selected through the office of NASMI as being representative of the range of processing and resulting emissions of the industry. Data obtained through this investigation were evaluated to quantitatively define emission control problems, reveal gaps in existing emission control technology, and develop concepts, to be considered for research and development.

REFERENCES TO DATA SOURCES

Data used in this study were obtained from plants of cooperating companies and from published sources. The industrial plant sources are treated confidentially and therefore not cited within the report. Published sources are cited within the report.

CHAPTER II

Process Raw Materials

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Chapter II

Process Raw Materials

Raw materials used in secondary zinc processing are zinc scrap materials, fluxes, and fuels for furnaces. These are described below.

ZINC SCRAP MATERIALS

For purposes of statistical presentation, one system of classification and nomenclature of zinc scrap materials has been developed and applied by the Bureau of Mines (Minerals YB). For purchase specification purposes, another system has been developed by NASMI and is applied within the industry (NASMI NF-66). These systems do not readily lend themselves directly for the technical analyses of this study, but are listed below to help describe the materials. For the technical analyses of this study, an additional system was formulated and is presented below. In this TECHNICAL CLASSIFICATION, zinc scrap materials are divided into two main catagories and the sub-classifications as shown under that heading.

BUREAU OF MINES CLASSIFICATION:

- New clippings
- Old zinc
- Engravers' plates
- Skimmings and ashes
- Sal skimmings
- Die-cast skimmings
- Galvanizers' dross
- Diecastings
- Rod and die scrap
- Flue dust
- Chemical residues

NASMI CLASSIFICATION:

Old zinc die cast scrap
New zinc die cast scrap
New plated zinc die cast scrap
Zinc die cast automotive grills
Old scrap zinc

New zinc clippings
Zinc die cast slabs or pigs
Galvanizers' slab zinc dross
Prime zinc die cast dross

TECHNICAL CLASSIFICATION:

A. Metallic Scrap. This scrap consists of metallic items, generally in the same shape as when manufactured or used.

1. Unplated zinc castings. Examples are reject castings, off-grade ingots, old castings, and printers plates. Castings in this classification are free of significant attachments made of other metals. They range from very clean castings to castings having relatively small amounts of oil and/or paint coatings, dirt, and other impurities.

2. Plated zinc castings. These are mainly automobile grills, having chromium platings. They are considered herein as having very little, if any, contamination with oils, paints, other organic materials, and dirt and only small amounts of higher melting-point metal attachments.

3. Zinc fabricating scrap. This scrap consists of that obtained from fabricating operations; examples are cuttings, punchings, chips, borings, turnings, and routings. They are considered here as being reasonably clean, except for coatings of oil or cutting compounds.

4. Contaminated zinc die-cast scrap. This scrap consists of assemblies containing zinc die-castings; attachments made of other metals; and materials that contain carbon compounds such as gaskets, electric insulation, and lubricants.

Examples are automobile fuel pumps, carburetors, horns, and washing machine parts. (Attachments made of metals having higher melting points than zinc may be referred to as "unmeltable attachments" or "unmeltables.")

B. Residual Scrap Materials. These are residues and impure alloys formed in the melting, fluxing, and application of molten-metal baths in galvanizing, die casting, and other processes. These materials are referred to, generally, as skimmings (or residues) and drosses. In this study, the terms skimmings and residues refer specifically to materials that form above metal bath surfaces. These materials are composed preponderantly of non-metallic substances including metal oxides and residual flux, with lesser amounts of metal contained as particles (or inclusions). They are of non-metallic appearance. The term dross, in this study, refers to materials that form within molten-metal baths, at top surfaces and at bottoms of melting vessels. They are composed mostly of metallic zinc and are metallic in appearance. As defined here, these terms are at variance with some industrial usage, as is noted below.

1. Skimmings (or residues).

a. Galvanizers' skimmings (ashes). This material is formed by oxidation of metal on galvanizing bath surfaces when no flux blanket is used. It is skimmed from above the molten metal bath surface. Skimmings are pulverulent, composed mostly of ZnO, with metallic inclusions. They are formed as galvanized items are withdrawn from baths, creating turbulence at the bath surface. Chlorine (as chlorides), derived from flux coatings on stock being galvanized, may be present in these skimmings in amounts from 0 to 12%. (The processing of "sal skimmings," formed on a galvanizing bath when a flux blanket is used, is not included in this study. See Chapter I.)

b. Die-cast skimmings. These materials are formed by accumulation of metal oxides, ZnCl and/or NH_4Cl flux, and other impurities above surfaces of zinc-alloy baths used for die-casting and are skimmed off. Skimmings are composed mostly of ZnO, with metallic inclusions making up 3 to 10%. Chlorine (as chlorides) ranges from 0 to 3% (approximately equivalent to 0 to 6% anhydrous $ZnCl_2$). The metallic inclusions are zinc, containing copper and aluminum, derived from die-cast alloy.

2. Dross

a. Top dross

(1) Galvanizers' top dross (also referred to as "galvanizers' top skimmings"). This material is formed by iron-aluminum compounds floating to the surface of galvanizing baths. These compounds result from reactions of aluminum with iron during certain galvanizing processes where aluminum is added to the baths to prevent a brittle layer from being formed in the coatings. They melt at a higher temperature and are lighter than zinc; therefore, they tend to separate and solidify at the bath surface. The product is skimmed from tops of baths and cast into chunks. It contains uncombined zinc and metal oxides, in addition to the aforementioned Fe-Al compounds. Top drosses contain around 90 to 95% Zn, 2 to 5% Al, are generally free of chloride flux but may contain small amounts.

(2) Die-cast dross. This material is formed at the top of die-casting process baths and is similar to galvanizers' top dross, but with different metal contents. Zinc content approximates 85%. Copper and aluminum are also present. There may be some chloride-flux content.

b. Bottom dross

(1) Galvanizers' dross. This material is formed by liquation of an iron-zinc compound to the bottom of galvanizing baths; this settling results from a higher specific gravity than zinc. In some galvanizing processes, dross may rest on a layer of molten lead. Removed from the bath with spoons and cast into chunks, the resultant product contains uncombined zinc in addition to the Fe-Zn compound. Some lead may also be present as well as chloride flux, the latter being picked up from the bath surface during dross removal.

(References: Nonferrous, pp. 63-74; Mathewson, pp. 315-21, 469)

FLUXES

The main fluxing materials used in secondary zinc processing are $ZnCl_2$ and NH_4Cl. These may be applied to the metallurigical process bath, or they may be contained in residual scrap as obtained, as noted in the foregoing description of those materials.

Other"smokeless fluxes" are in limited usage for processing relatively clean scrap. Cost is considered too high and effectiveness in emission control too limited to provide solutions to general processing and emission control problems. Application of these fluxes does not appear to fall within the problem area of this study and is therefore dismissed from further consideration in this report.

FUELS

Natural gas and fuel oil are the principal fuels used in secondary zinc processing. Based on the operations of plants visited during this study, it is believed that the fuel used most is natural gas. Oil is used in smaller facilities and as a standby fuel. Electricity is sometimes used to heat furnaces. This use of electricity appears to be unusual and limited to processing clean scrap that does not pose air pollution problems.

Chapter III

Products of Processes

Products of secondary zinc plants are listed and defined as follows:

A. Specification zinc alloys. Standard alloys, such as die-casting types, produced by sweat-processing and re-alloying zinc metallic scrap.

B. Zinc-content metal. Zinc-containing metal produced by sweat-processing metallic and residual zinc scrap material in preparation for distillation.

C. Distilled slab zinc. Zinc-containing metal approaching 100% Zn purity produced by distillation of metal derived from zinc scrap materials.

D. Zinc dust. Zinc-containing metal produced by distillation of metal derived from zinc scrap materials. The distilled zinc vapor is allowed to condense under conditions which form small spherical particles.

E. Zinc Oxide. ZnO approaching 100% purity produced by distillation of scrap-derived zinc with subsequent oxidation of vapor by atmospheric combustion.

F. By-product residues containing ZnO (for reduction to metallic zinc by primary smelters).

1. Sweat-process residues. These are residues that remain after metal has been extracted from metallic or residual zinc-scrap material. Some chloride flux may be retained in these residues.

2. Residues from water-wash pre-treatment of residual zinc-scrap material, applied to extract metal inclusions. These may be chemically treated and/or calcined to reduce chloride content. (See PRE-TREATMENTS, Chapter IV)

G. By-product particulates containing ZnO (for agricultural soil treatment). These are emitted particulates collected by control equipment (usually baghouses) having a maximum chloride content of 5%. Commercial usage of collected particulates has not been determined for collected particulates having over 5% chloride content.

H. By-product distillation residues containing Al and Cu (for use in aluminum alloying). These are removed from distillation furnaces.

I. Ferrous and non-ferrous unmeltable attachments to zinc base die castings.

Chapter IV

Summary of Processes, Process Effluents and Emission Points

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Chapter IV

Summary of Processes, Process Effluents and Emission Points

PRETREATMENTS

Treatments, preliminary to melting operations, are applied to some types of zinc-scrap material.

Attachments that are accessible and can be removed easily are removed from contaminated zinc die-cast scrap. Attachments and impurities that are often not removed include gaskets, sealed-in lubricants, screws, and electrical parts. Considerable organic materials and metals, other than zinc, are therefore retained in this scrap when it is charged to melting (sweating) furnaces.

Concentration of metallic zinc in skimmings is increased by ball-mill pulverizing, followed by pneumatic treatment and/or screening to remove part of the pulverulent, non-metallic constituents.

In some instances, skimmings are crushed and then treated in the following manner. The crushed skimmings are washed with water to separate non-metals as a slurry and allow zinciferous metal particles to settle out; the slurry is then treated with Na_2CO_3 to convert chlorides (mainly $ZnCl_2$) to NaCl, forming insoluble $Zn(OH)_2$. Most of the NaCl is separated from the insoluble residues by filtration and settling; the residue is dried and calcined in a kiln to convert $Zn(OH)_2$ to ZnO by driving off H_2O and vaporizing any remaining $ZnCl_2$. The calcined product is mostly ZnO and is suitable for smelting. The kiln fume is collected in polyester fabric bag filters and recycled.

Emissions from the aforementioned pretreating processes were not studied in depth during this investigation, since it did not appear that there were notable difficulties in their control, there being no reports from industrial representatives indicating any problems. These emissions are therefore not dealt with further in this report.

SWEAT PROCESSES

In sweat processing, heat is applied to scrap materials, which may be of either the metallic or residual types, to melt and separate metallic zinc from metal attachments, having higher melting points, and from non-metallic residues. Any organic materials in scrap are also burned off during sweating. Sweat processing is accomplished by charging the scrap into a melting furnace. The charge may be worked, by agitation or stirring during melting; and chloride flux may be present either as residual flux, in charged residual scrap, or as flux added to the charge. Working and fluxing of the charge are done to help effect the desired metal separation. A molten-metal bath is formed from the metallic zinc (with dissolved alloy metals). Non-metallic residues, along with some platings, form above the molten-metal bath surface and are skimmed off. Unmeltable attachments settle to the bottom and are removed. The molten metal may then be (1) cast directly into blocks for subsequent further processing, or (2) fed directly to a distillation furnace, or (3) it may be sampled and analyzed, and then alloyed by adding metals to obtain specification composition, and then cast as ingots.

Types of furnaces used for sweating zinc-scrap materials are discussed in the following order:

1. Melting-kettle (or kettle) furnaces
2. Reverberatory furnaces
3. Rotary furnaces

4. Muffle furnaces
5. Electric-resistance furnaces

Of these, most usage is of the first three, which are therefore given principal attention in this chapter. Figures 4-1 and 4-2 are schematic flow diagrams that show sweat processing in kettle and reverberatory furnaces. The rotary furnace is, in effect, a mechanical modificatiin of the reverberatory furnace, as will become apparent in the description of that furnace in a subsequent paragraph. Emission points of sweat furnaces and effluents emitted from those points are shown in Table IV-1. These furnaces, their applications, emission points, and effluents are described further in the paragraphs below.

KETTLE FURNACE

The kettle furnace consists of a melting vessel (kettle), made of cast iron in most cases, mounted over a combustion chamber. Scrap materials, which may include metallic and/or residual types, are charged into the kettle. The metallurgical-process bath is formed as zinciferous metal is melted and residues form above the molten-metal surface. Operating temperatures of kettle-process baths range from 800 to 1000°F. Production is on a batch basis, with one process heat requiring around 6 to 8 hours to process and pour. A molten heel may be retained as finished alloy is removed from furnaces and additional scrap (process material) charged.

Normally, products of fuel combustion are exhausted separately from emissions of the metallurgical-process bath, through separate venting of the combustion chamber. Natural gas is the generally used fuel (fuel oil being used in a smaller number of cases).

As noted previously, sweat processing in a kettle furnace is shown schematically in Figure 4-1, along with emissions and emission points. Emission points and effluents emitted from these points are detailed further in Table IV-1.

REVERBERATORY FURNACE

The reverberatory furnace has a general box configuration with a sloped bottom (hearth). It is used to process both metallic and residual zinc scrap materials, which are charged into the furnace and rest on the hearth. Burners are located in the upper part of the furnace; combustion of fuel above the charge supplies heat to burn off organic substances, as well as heat to melt the zinc alloys in the charge. Furnaces are designed and burners are positioned to minimize flame impingement on the charge and to reduce oxidation and entrainment of metal oxide particles in emissions. As zinc alloys melt, they separate from unmeltables and flow downward over the hearth. Bath temperatures in reverberatory furnaces are usually around 1000°F. When comparable materials are processed, these baths are usually maintained at higher temperatures than kettle-furnace baths to increase fluidity of molten metal and thereby improve separation from unmeltables. Metal flows from the furnace as it melts; and, at intervals, unmeltables are raked out and additional process material charged.

Reverberatory furnaces may be independent units or they may be integral with distillation furnaces (Figure 205, APEM). Consideration here is limited to the independent type of unit where molten metal from the hearth flows through a spout into ladles or kettles. The metal may then be processed further to obtain a specification alloy, or it may be fed to a distillation furnace. Integral sweating-and-distillation furnaces are discussed further in a subsequent section on distillation furnaces.

Sweat processing in a reverberatory furnace is shown schematically in Figure 4-2, along with emissions and emission points. These emission points and effluents from these points are detailed further in Table IV-1. It might be noted that the pouring spout of the reverberatory furnace is not listed as an emission point; the molten-metal temperature at this point is normally not high enough to vaporize significant amounts of zinc (APEM p. 294).

ROTARY FURNACE

The melting unit of the rotary-type furnace consists of a hollow cylinder mounted with its lengthwise axis sloped at a small angle from horizontal. During operation, this cylinder is mechanically rotated on that axis and internally heated by gas or oil burners. The principal application of the rotary furnaces at plants visited during this study was for processing contaminated die-cast scrap, without application of fluxing compounds. Scrap materials are fed into the high end of the melting cylinder. As the cylinder rotates, zinc melts and flows out through openings in the low end, usually into a kettle where residues are skimmed off. Unmeltables are separated from the bath by tumbling them out of the low end of the cylinder or by manual raking and scraping. Rotary-furnace bath temperatures are usually lower than those of kettle or reverberatory furnaces because rotation helps (1) separate molten zinc from unmeltables, (2) maintain molten zinc and alloy metals in solution, and (3) use heat more efficiently by avoiding localized high temperature zones, thereby allowing lower bath temperatures to be applied. The collected zinc-containing metal may then be transferred to a distillation furnace, or its composition may be adjusted to an alloy specification.

Observations of this study indicated no visible (or significant) emissions at the low end of the cylinder as the molten metal or unmeltables flow from or are being removed from the melting cylinder.

The only emission point noted (in Table IV-1) is therefore, the furnace flue (the high end of the melting cylinder). Emissions from this point are those contained in furnace-exhaust effluent (flue gas), which consists of the same types of constituents as those listed for furnace flue effluents from reverberatory furnaces, except that emissions derived from flux would not normally be contained in rotary-furnace effluent.

MUFFLE FURNACE

In the muffle furnace, as applied to sweating processes, combustion gases are separated from charged zinc-scrap materials by a "muffle". (The same principle is applied to distillation as shown in Figure 204 of APEM.) This design permits separation of combustion products from those emissions derived from charged zinc-scrap materials and flux. In this respect, the muffle furnace is similar to the kettle furnace. Findings of this study indicate little usage of the muffle furnace for sweating (although usage for distillation is significant). Probably this limited usage is due to low thermal efficiency. Because usage is not extensive, the muffle furnace as applied to sweat processing is not subjected to detailed analysis in this study.

ELECTRIC-RESISTANCE FURNACE

Findings of this study indicate that electric-resistance furnaces are used in a small number of plants for processing clean, scrap-derived zinc metal, and that processing such scrap does not pose significant air-pollution problems regardless of furnace type. It appears that by avoiding fuel-combustion products, application of electric-resistance furnaces might have an emission-control advantage. However, cost of electric energy probably precludes usage of electric-resistance furnaces for sweat processing in nearly all situations (except for melting clean metal). This type of furnace is therefore not subjected to detailed analysis in this study.

DISTILLATION PROCESSES

Distillation processes are of several variations (APEM pp. 296-9; Mathewson p. 317) which can be reasonably represented by the retort furnace system and the muffle furnace system. Figures 203 and 204 of APEM show examples of distillation processing by means of these systems. Table IV-2 of this report details their emission points and the effluents emitted. Further description is provided in the paragraphs below.

RETORT FURNACE SYSTEM

The retort furnace system consists of two units: (1) a retort furnace and (2) a condenser (Figure 203, APEM). In the retort furnace, the distillation retort (which may be bottle-shaped) is mounted inside the furnace closure where fuel is burned, heating the retort and its content. The charge to the retort may consist of molten-zinc-rich metal obtained directly from a sweat furnace, cast zinc-content metal from a zinc-sweat process, or zinc redross. Zinc is vaporized in the retort, and the vapor passes through a refactory pipe to a condenser, where it may be condensed either as zinc dust or molten zinc (for casting into slabs), depending on the type of condenser used. The condenser for making zinc dust consists of a bare sheet-steel shell. Zinc vapor entering this condenser cools rapidly and therefore condenses into small particles. The condenser for making slab zinc also consists of a steel shell, but is refractory lined for thermal insulation. Zinc vapor entering this condenser cools more slowly, forming liquid metal on internal surfaces of the refractory lining; the liquid metal flows to the bottom where it is tapped at intervals and cast into slabs.

Retort furnaces may also be used to produce zinc oxide by allowing zinc vapor, from the retort, to burn in air, and collecting the resulting ZnO product in a baghouse.

Distillation residues (mainly mixtures of aluminum and copper) are raked out of the retort immediately after each distillation heat is completed, while residues are still at a high temperature.

Fuel-combustion products are exhausted independently of any emissions from the retort charge.

Emission points in the retort-furnace system are listed, with emissions from those points, in Table IV-2 and are discussed further as follows:

A. Retort opening. During removal of distillation residues from the retort, ZnO particles are emitted as the molten zinc that remains in the residues continues to vaporize and oxidize. Ambient air composes the gaseous part of effluent formed at this point.

B. Pressure-relief valve or "speise" hole of condenser. One or the other of these devices is used to retain a positive pressure and exclude air from condensers (APEM p. 297). Emissions from the "speise" hole consist of nearly-pure ZnO. Emissions from condenser relief valves are mixtures of zinc dust and ZnO. In heats where dross is contained in the retort charge, a small amount of chloride particulates, derived from residual flux, might also be emitted at these points. Ambient air composes the gaseous part of effluents formed at these points.

MUFFLE FURNACE SYSTEM

The muffle-furnace system consists of a melting unit (reverberatory furnace) and a vaporizing unit (muffle furnace), combined in an integral structure, and includes a condenser (APEM p. 298). Materials such as contaminated zinc die-cast scrap are charged into the melting unit. As zinc alloys melt, the molten metal flows from that unit to the bottom of the vaporizing unit. Fuel combustion in the vaporizing unit takes place in the upper chamber of that unit, which is separated from the molten metal and zinc vapor (in the lower chamber) by an arched partition (muffle). Combustion gas from the upper chamber is exhausted to the melting unit, adding heat to that of melting unit burners to help melt the charged scrap material. Zinc vapor is channeled from the vaporizing unit to the condenser where it is partly condensed to liquid metal and cast as slabs. The non-condensed vapor is oxidized to ZnO, which is collected in a baghouse.

The melting unit is charged at one end; and unmeltable attachments and skimmings are removed from the other. Flux is not applied to, or contained in, the melting-unit charge.

In the melting unit incineration of organic materials in charged metallic scrap is virtually complete so as to prevent emission of carbonaceous particulates in significant amounts.

A vibrating screen is used at the discharge end of the melting unit to separate skimmings from unmeltables after removal from the unit. This device is a source of considerable amounts of particulate (mainly ZnO) emissions (APEM p. 299).

Emission points and effluents from the muffle-furnace system are detailed in Table IV-2.

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Fig. 4-1 - Sweat Processing of Zinc-Scrap Materials in Kettle Melting Furnace

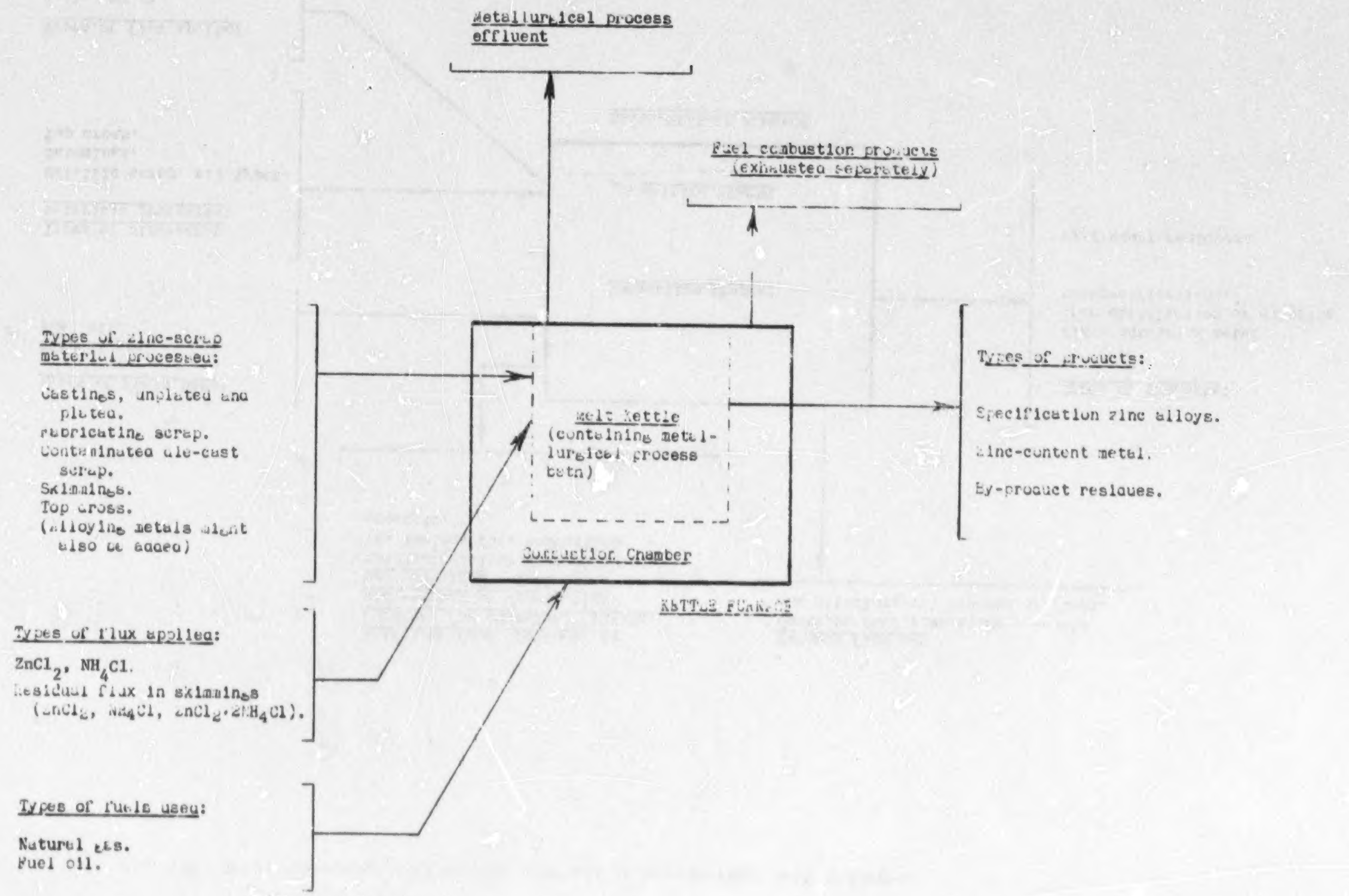
Metallurgical process effluent
Fuel combustion products (exhausted separately)
Types of zinc-scrap material processed:
Castings, unplated and plated.
Fabricating scrap.
Contaminated die-cast scrap.
Skimmings.
Top cross.
(Alloying metals might also be added)
Melt Kettle (containing metallurgical process bath)
Combustion Chamber
KETTLE FURNACE
Types of products:
Specification zinc alloys.
Zinc-content metal.
By-product residues.
Types of flux applied:
$ZnCl_2$, NH_4Cl.
Residual flux in skimmings ($ZnCl_2$, NH_4Cl, $ZnCl_2 \cdot 2NH_4Cl$).
Types of fuels used:
Natural gas.
Fuel oil.

Fig. 4-2 - Sweat Processing of Zinc-Scrap Materials in Reverberatory Melting Furnace

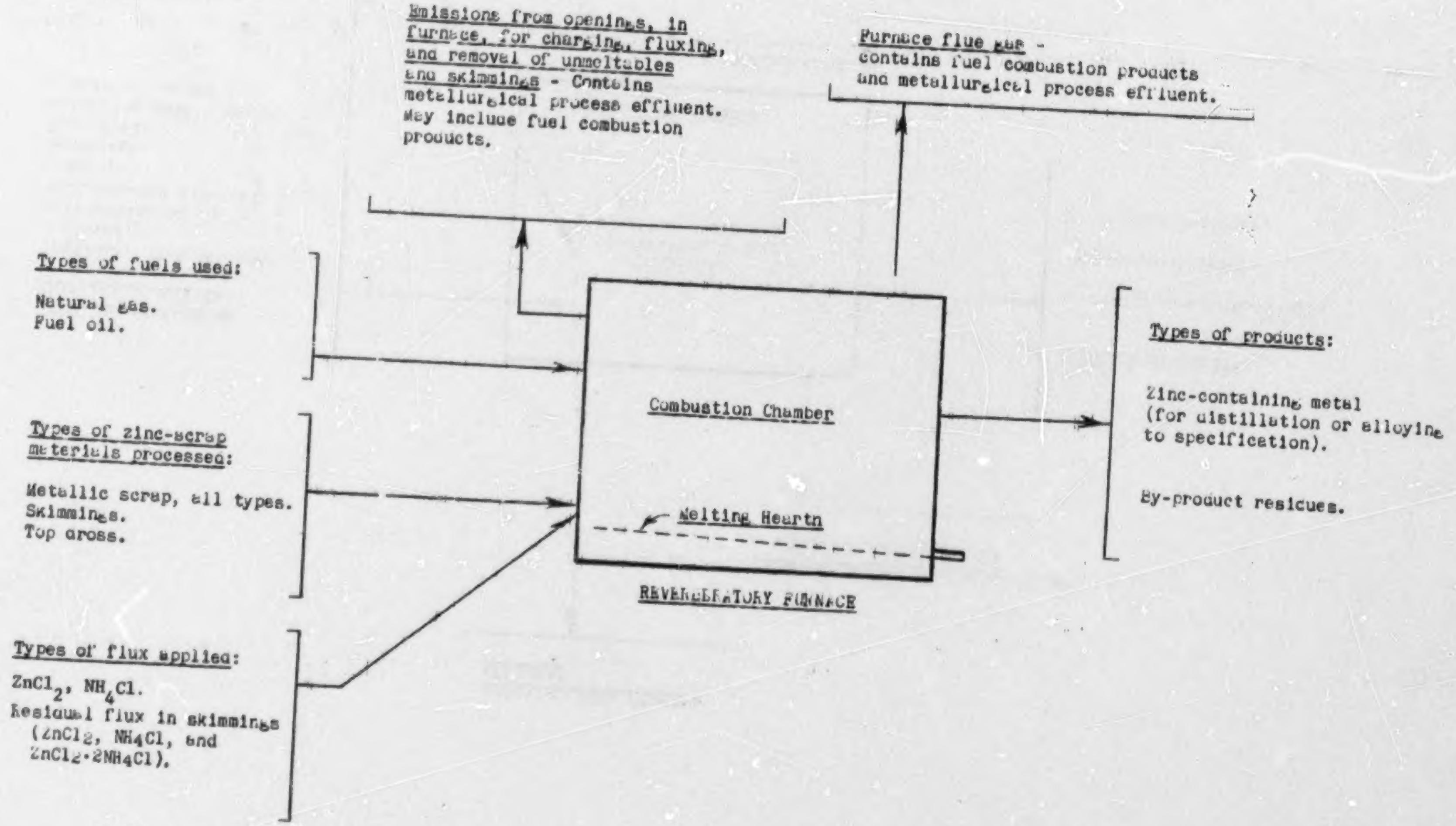
Emissions from openings, in furnace, for charging, fluxing, and removal of unmeltables and skimmings - Contains metallurgical process effluent. May include fuel combustion products.
Furnace flue gas - contains fuel combustion products and metallurgical process effluent.
Types of fuels used:
Natural gas.
Fuel oil.
Types of zinc-scrap materials processed:
Metallic scrap, all types.
Skimmings.
Top dross.
Types of flux applied:
$ZnCl_2$, NH_4Cl.
Residual flux in skimmings ($ZnCl_2$, NH_4Cl, and $ZnCl_2 \cdot 2NH_4Cl$).
Combustion Chamber
Melting Hearth
REVERBERATORY FURNACE
Types of products:
Zinc-containing metal (for distillation or alloying to specification).
By-product residues.

TABLE IV-1 _ EMISSION POINTS AND EFFLUENTS OF SECONDARY ZINC-SWEAT PROCESSES

Process (defined by type of furnace used)	Emitting Process Equipment Unit	Emission Point of Process Equipment Unit	Constituents of Effluents from Emission Points
Kettle Furnace	Melt Kettle	Top of melt kettle (or surface of metallurgical process bath, formed from charge).	A. Emissions from process charge. 1. Products of combustion or thermal decomposition of organic materials in charge. 2. Emissions derived from metals, fluxes, and residues in metallurgical process bath, including metal oxides resulting from presence of air contacting metal. B. Air induced or infiltrated into exhaust effluent stream.
	Combustion chamber	Combustion chamber vent	A. Products of combustion of fuel (usually natural gas).
Reverberatory Furnace	Combustion chamber, containing melting hearth. (May also be referred to as "sweating chamber").	Furnace flue (exhausting combustion chamber).	A. 1.-2. Emissions from process charge (same items as listed above). B. Air induced or infiltrated into furnace, thence into flue. (would be in excess of air consumed in combustion). C. Products of combustion of fuel (usually natural gas).
		Openings for charging and fluxing; and removal of unmeltables and skimmings.	A. 1.-2.; B.; and C. -Same items as listed above for furnace flue. These effluents are formed from (1) gases escaping from the furnace; (2) emissions from the molten metal and skimmings being withdrawn from furnace with unmeltables; and (3)ambient air.
Rotary Furnace	Rotating, cylindrical melt unit. (May also be referred to as "sweating chamber" or "combustion chamber").	Furnace flue (high end of melting cylinder).	A. 1.-2.; B.; and C. -Same as listed above for flue of reverberatory furnace, except emissions derived from flux are not normally contained in rotary furnace effluent.

TABLE IV-2 (page 1 of 2) EMISSION POINTS AND EFFLUENTS OF SECONDARY ZINC-DISTILLATION PROCESSES

Process (defined by furnace system used)	Emitting Process Equipment Unit	Emission Point of Process Equipment Unit	Constituents of Effluents from Emission Points
Retort Furnace System (See Fig. 203, APEM)	Distillation Retort	Opening of distillation retort. (Emissions occur during removal of distillation residues. This opening may be referred to as "charging hole". It is used for applying charge to retort and removing residues).	A. Emissions from distillation residues. 1. ZnO (makes up most of emitted particulates). 2. Oxides of other metals (mainly Al_2O_3) - small amount. B. Ambient air.
	Combustion chamber	Combustion chamber vent.	A. Products of combustion of fuel (usually natural gas).
	Condenser	Pressure relief valve. (Used to retain positive pressure and exclude air from condenser).	A. Emissions from vapors distilled from retort charge, partly oxidized by residual air in retort-and-condenser system. 1. ZnO particulate. 2. Metallic zinc dust (particulate). 3. Chloride particulates, derived from flux. (Very small amounts may occur when dross is charged to retort). B. N_2 from residual air in retort and condenser.
	Condenser	"Speise" hole. (Used instead of pressure relief valve for same purpose. Zn vapor escaping from condenser thru speise hole is ignited in air, producing ZnO particulates).	A. Emissions from vapors distilled from retort charge and oxidized. 1. ZnO particulate, nearly pure. (The charge to retort is of molten metal which would not produce chloride emissions - APEM p. 296). B. N_2 from residual air in retort and condenser. C. Ambient air

TABLE IV-2 (page 2 of 2) EMISSION POINTS AND EFFLUENTS OF SECONDARY ZINC-DISTILLATION PROCESSES

Process (defined by furnace system used)	Emitting Process Equipment Unit	Emission Point of Process Equipment Unit	Constituents of Effluents from Emission Points
Muffle Furnace System (See Fig's. 204-5, APEM)	Melt Unit (reverberatory furnace)	Flue of melt-unit combustion chamber.	A. Emissions from melt-unit charge. 1. Products of combustion or thermal decomposition of organic materials in charge. 2. Emissions derived from metals and residues (usually no flux) in metallurgical-process bath, including metal oxides resulting from presence of air. B. Air induced or infiltrated into melt unit, thence into flue. (Would be in excess of air consumed in combustion). C. Products of combustion of fuel (usually natural gas), burned in melt unit and vaporizing unit.
		Openings in melt unit for charging scrap material and removing unmeltables and skimmings.	A. 1., 2.; B.; and C. -Same items as listed above for furnace flue. These effluents are formed from (1) gases escaping from the melt unit; (2) emissions from the molten metal and skimmings being withdrawn from melt unit with unmeltables; and (3) ambient air.
	Vaporizing Unit (muffle furnace)	Tap hole of vaporizing unit. (Emissions occur during removal of distillation residue).	A. Emissions from distillation residues. 1. ZnO particulate, nearly pure (APEM p. 299) B. Ambient air.

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Chapter V

Analysis of Emitting Processes and Development of Hypothesis on Emission Generation

PROCESSES SELECTED FOR ANALYSIS

As shown in Chapter IV, chloride fluxes and organic materials are contained in charges to zinc-sweat furnaces in quantities that may be substantial. By comparison, very little if any flux and no organic materials are contained in charges to retorts or vaporizing units of distillation furnaces. Chloride emissions are derived from chloride fluxes and carbonaceous emissions from organic materials in furnace charges. Exhaust effluents from zinc-sweat processes may therefore contain substantial amounts of chlorides, as well as carbonaceous substances; very little chlorides and no carbonaceous substances are contained in emissions from distillation processes. Therefore, in this analysis, attention is confined to the operations that make up zinc-sweat processes, the materials entering into those processes, and the resulting emissions. It is noted, however, that because of zinciferous constituents common to emissions from both zinc-sweat and zinc-distillation processes, certain technological factors are common to controlling emissions from both types of processes. For this reason, distillation process emissions and their control will be discussed in later chapters. In this way, emission control technology for all secondary zinc processes will be considered together where there is common applicability.

DEFINITIONS OF TERMS EMPLOYED IN ANALYSIS

Effluent. The term "effluent" or "exhaust effluent" refers to the gas stream that flows from the region of the charge or bath being processed in a melting (sweating) furnace, and is then exhausted from the furnace. The effluent includes any particulate or gaseous emissions derived from the charge and any atmospheric air that enters the effluent stream. Fuel combustion products that are mixed into that stream also become a part of the effluent. Thus, combustion products of fuel consumed in reverberatory and rotary furnaces are part of the effluent; combustion products of fuels consumed in kettle furnaces are exhausted separately and are not part of the effluent. Fuel combustion products occuring by themselves are not within the problem area of this study, and are therefore not included in this definition or the following analysis.

Infiltrated air. The term "infiltrated air" refers to all atmospheric air that enters the effluent. It includes (1) air induced into the effluent by the furnace draft, (2) excess combustion air in reverberatory and rotary furnaces, and (3) air that mixes with emissions escaping from furnace openings used for charging, removing unmeltables, etc.

Metallurgical-process bath. The term "metallurgical-process bath" or "process bath" refers to the bath formed during zinc-sweat processing, which includes molten metal, residues, and any flux present. (Flux in the process bath is understood to fuse with residues, the fused mixture tending to float to the bath surface.)

Molten-metal bath. This term refers to the molten-metal portion of the metallurgical-process bath.

Emitting process-equipment unit. This term refers to the process-equipment unit in which emissions are generated. In the kettle-sweat furnace, this unit would be the melting kettle. In the reverberatory or rotary furnace, it would be the combustion (sweating or melting) chamber. (See figures 4-1, 2 and Table IV-1.)

PROCESS OPERATIONS THAT EFFECT EMISSIONS

For the purpose of analyzing emissions, the operations that make up all zinc-sweat processes are considered in two phases: (1) Melting the charge, and (2) Fluxing and working the metallurgical-process bath. These operations may be conducted sequentially, the first preceding the second, or partly or wholly concurrently. Each phase is briefly summarized and related to furnace applications.

Melting the Charge. To recover metallic zinc, scrap materials are heated to temperatures between 800 and 1100°F. In this temperature range, zinc is melted and alloy metals are retained in the molten-metal bath. Heat may be applied by conduction, as in kettle and electric-resistance furnaces. Heat may also be applied by a combination of convection and radiation, as in reverberatory and rotary furnaces. In the latter two furnaces, convection heating results from hot fuel combustion gases being circulated in the charge region, whereas radiant heating results from the furnace walls being heated by the same hot gases then radiating heat to the charge. Also, heat may be applied to the charge mainly by radiation, as in muffle furnaces.

Fluxing and Working the Metallurgical-Process Bath. Flux may be applied to the charge before melting (where present in residual scrap composing part or all of the charge), or it may be applied during or after melting. The process bath may be worked by stirring or agitating to fuse and blend zinc and alloy metals into a contiguous molten-metal bath and separate the residue-flux mixture (skimmings) and unmeltables from that bath. Both fluxing and working of process baths may be done in kettle and reverberatory furnaces, in single heats. Working of baths, usually without fluxing, is done in rotary furnaces. (See Chapter IV.)

MATERIALS AND FUELS APPLIED TO EMITTING PROCESS-EQUIPMENT UNITS

In the following paragraphs, materials and fuels that are applied to sweat furnaces and that might materially affect emissions are analyzed to determine their constituents and provide a basis for a hypothesis on how emissions are generated and of what they are composed.

ORGANIC CONSTITUENTS OF CHARGES

Materials made of organic compounds may be present in charged metallic scrap. Examples are gaskets, fabrics, electrical insulation, paper, and lubricants. Although these compounds are mainly of carbon, hydrogen, and oxygen, other elements could be present:

A. Sulfur in natural rubber and polysulfide polymers.
B. Chlorine in chloroprene and vinyl polymers.
C. Nitrogen in nitrile rubbers, polyamide plastics, and protein binders.
D. Fluorine in fluorocarbon plastics and fluorinated elastomers.
E. Silicon in silicone rubbers and lubricants.

emissions from certain sweat processes. No special problems were reported or indicated involving the other elements listed (A through E). For that reason, quantities of these elements in emissions are believed to be small, and it is therefore assumed here that organic materials contained in furnace charges are essentially composed entirely of carbon-hydrogen-oxygen compounds.

METALLIC CONSTITUENTS OF CHARGES AND RESULTING COMPOSITION OF MOLTEN METAL BATHS

In all of the types of scrap materials that are charged to zinc sweat furnaces (see Chapter II), metallic zinc is derived mainly from die-casting and galvanizing alloys with these typical compositions:

A. Die-cast alloys - 94% Zn, 4% Al, 1% Cu, and 0.05% Mg; with restrictions to maximum of 0.1% Fe, 0.007% Pb, 0.005% Cd, and 0.005% Sn.

B. Galvanizing alloys - Restricted to a minimum of 98.3% Zn, and maximums of 0.08% Fe and 1.6% Pb.

Die-cast alloys may be contained in both metallic and residual scrap. Galvanizing alloys are contained only in residual scrap.

Very small amounts of nickel may be present in residual scrap, probably derived from alloy cast-iron melting vessels and from platings. (Mathewson, pp. 387-8, 486,315).

The assumption is made here that chromium platings, which may be contained in charges, are essentially inert and insoluble at process bath temperatures. It is therefore considered that they do not significantly affect emissions, although traces of chromium might be emitted.

It is also assumed that unmeltable attachments essentially separate from the process bath and do not significantly affect emissions. It is noted, however, that small quantities of metals in these attachments, such as copper, might dissolve in the molten metal.

Galvanizing alloys contain a higher percentage of lead than die-cast alloys. This study, however, indicated no special emission problems caused by lead. Pertaining to the possible emission of lead vapor, the boiling points of lead and zinc, 3160 and 1665°F respectively, indicate that any emission of lead vapor during zinc-sweat processes would be very small. Further, as a relatively unreactive metal, lead contained in process baths probably would not form compounds that would be emitted in significant quantity.

Findings of this study indicated that scrap materials containing die-casting alloys are more representative of materials subjected to sweat processing where charges contain significant amounts of flux than those containing galvanizing alloys. Galvanizers' skimmings are pretreated to remove residual flux, producing clean zinciferous metals particles that can be distilled directly or sweated with little or no flux being applied. Galvanizers drosses that contain little or no residual flux are either distilled directly or sweated without applying flux.

These considerations indicate that the composition shown below would be very representative of molten-metal baths obtained from sweat processing, where the charge contains significant amounts of flux:

Metal	% by Weight of Metal Bath Formed During Sweat Processing
Zn	94%
Al	4%
Cu	1%
Fe	0.1%
Mg	0.05%
Pb	Less than 0.01% each
Sn	
Ni	
Cd	
Cr	

FLUXING COMPOUNDS IN CHARGES

Fluxing compounds are considered in this study as consisting of $ZnCl_2$ and/or NH_4Cl. The double salt, zinc ammonium chloride ($ZnCl_2 \cdot 2NH_4Cl$) could be contained in residual scrap materials. This salt is assumed here as equivalent to uncombined $ZnCl_2$ and NH_4Cl, undergoing the same reactions and physical changes during zinc-sweat processing.

INORGANIC IMPURITIES IN CHARGES

As applied in this report, the term "inorganic impurities" does not include uncombined metals. It is assumed that inorganic impurities consist essentially of oxides of the metals present, particularly ZnO. This assumption is believed to approximate actual conditions. However, accumulations of dirt, residues from phosphate and chromate metal-finishing treatments, fillers and pigments of rubbers, plastics, and paints (including compounds of Si, Ti, Sn, Cr, Ca, Cd, and Fe) could also be present.

FURNACE FUELS

Gas or oil of 100% hydrocarbon composition are considered as being used for all process fuel combustion. Sulfur content is assumed negligible.

EMISSIONS - THEIR GENERATION AND COMPOSITION

The following paragraphs present a theoretical analysis of the effects on emissions of the process operations, materials, and fuels (enumerated and described earlier in this chapter) that are applied to zinc-sweat processes. A hypothesis is developed, based on this analysis, on how emissions are generated and of what they are composed. The analysis incorporates certain assumptions, which are believed to represent actual occurrences and conditions. In a later chaper the hypothesis developed here is applied in interpreting data obtained from emission tests and thus is subjected to verification.

CONSTITUENTS THAT MAKE UP EFFLUENT

Generally, any carbonaceous emissions in effluents occur during melting operations when organic materials in the charge are burned off. Noncarbonaceous emissions occur during fluxing and working operations when vaporization, oxidation, and entrainment involving constituents of the process bath and surrounding gases take place. Emission of ZnO particulates (noncarbonaceous emissions) may also take place during melting of the charge due to vaporization and oxidation of elemental zinc taking place in kettle and reverberatory furnaces (particularly in the latter) during that phase of the process.

Considering sweat processing in kettle, reverberatory, and rotary furnaces, organic materials might be contained in charges to all of these. On the other hand, flux might be contained in charges to kettle and reverberatory but not normally in charges to rotary furnaces. It then follows that the possible combinations of constituents making up effluents from these furnaces may be listed as follows:

Furnace Type	Constituents of which Effluents may be Formed
Kettle *	Carbonaceous emissions from the charge, during melting. Noncarbonaceous emissions from (1) the charge during melting and (2) the metallurgical process bath. Could include chlorides. Infiltrated air.
Reverberatory	Carbonaceous emissions from the charge, during melting. Noncarbonaceous emissions from (1) the charge, during melting and (2) the metallurgical process bath. Could include chlorides. Infiltrated air. Fuel combustion products.
Rotary	Carbonaceous emissions from the charge, during melting. Noncarbonaceous emissions from (1) the charge, during melting and (2) the metallurgical process bath, without flux. No Chlorides contained in emissions. Infiltrated air. Fuel combustion products.

Detailed consideration is given below to the generation and composition of carbonaceous and noncarbonaceous emissions, and fuel combustion products, which along with infiltrated air make up effluents as shown in the above tabulation.

---

[*] Fuel combustion products from kettle furnaces are exhausted separately from the effluent that flows from the process bath, and are therefore not listed here. (See Effluent definition, page V-2)

All of the considerations below apply to sweat processing in kettle and reverberatory furnaces where chloride flux is included in charged process materials. The considerations that pertain to noncarbonaceous emissions do not apply to rotary furnaces, since chlorides, derived from flux, are not normally emitted from those furnaces. Also, findings of this study indicate that because of lower bath temperatures and absence of flux in rotary furnaces, noncarbonaceous emissions from that type of furnace are not significant. Rotary furnace emissions are therefore considered here as being entirely carbonaceous under usual process conditions.

GENERATION OF CARBONACEOUS EMISSIONS FROM CHARGE

As material charged to furnaces is heated, metal melts and any organic compounds present undergo decomposition, oxidation, vaporization, and/or mechanical entrainment into the exhaust effluent gas stream. Carbonaceous emissions thus formed are cooled by infiltrated air and radiation of heat from ducts carrying the effluent. Where emission control equipment is used, cooling may also occur in that equipment, such as through the cooling action of a scrubbing fluid. Finally emissions may be cooled when effluent is exhausted to the atmosphere. During cooling, carbonaceous vapors condense, and viscosities of liquids increase. Resulting carbonaceous emissions may therefore be composed of combinations of carbonaceous fly ash, solid carbon particles, liquid droplets of carbon compounds having consistencies ranging from oily to tarlike, and gaseous carbon compounds. It follows, from considerations of organic constituents of charges, that these emissions would be made up essentially of inert ash and compounds of carbon, hydrogen, and oxygen.

GENERATION OF NONCARBONACEOUS EMISSIONS FROM CHARGE

As a process bath is fluxed and worked, noncarbonaceous emissions may result from chemical reactions and physical occurences involving the following substances:

A. Fluxes applied to bath or contained in charged residual scrap.

B. Metals in molten-metal bath.

C. Residues that accumulate (fused or mixed with any flux present) at the top of the process bath above the molten metal, these residues being introduced as inorganic impurities in the charge or formed by oxidation of charged metal.

D. Oxygen in infiltrated air. (Atmospheric nitrogen is not considered as a possible reactant because it is normally unreactive at zinc-sweat process temperatures.)

Fluxes consist of $ZnCl_2$ and/or NH_4Cl. Metals contained in the molten-metal bath are considered in the subsequent analysis as being limited to zinc and aluminum. This simplification is justified by data, shown previously, indicating that other metals would not be present in sufficient quantities to significantly affect the nature or amount of emissions. For similar reasons, metal oxides in residues are considered as consisting of ZnO and Al_2O_3. It is immediately apparent that $AlCl_3$ might be produced within the process bath by reactions of $ZnCl_2$ with aluminum (APEM, p. 287). It follows from these considerations that the metals and compounds in process baths that may enter into chemical reactions and physical occurences forming noncarbonaceous emissions consist essentially of Zn, Al, NH_4Cl, $ZnCl_2$, $AlCl_3$, ZnO, and Al_2O_3. Physical properties of these materials that pertain to emissions are tabulated in Table V-1 and shown graphically in Figure 5-1.

Vapor pressures plotted in Figure 5-1 show that at the temperature of molten metal, NH_4Cl would vaporize at a high rate and that $ZnCl_2$ and metallic zinc would also vaporize significantly. Data in Table V-1 show that ZnO and Al_2O_3 are refractory at the temperatures of the process bath. Therefore, any ZnO or Al_2O_3 in residues would not vaporize but might enter the effluent by mechanical entrainment due to the velocity of the effluent stream. Agitation and skimming of the process bath would promote vaporization of metal and flux as well as mechanical entrainment of residue particles into the effluent. Also in this temperature range, NH_4Cl decomposes to NH_3 and HCl gases, which may recombine when cooled, by infiltrated air, forming small particles of NH_4Cl fume (APEM, p. 294).

Owing to the presence of the molten metal, vapors and gases formed as noted above, the following reactions could take place in the immediate region of the molten metal bath surface:

(1) NH_4Cl (flux) → NH_3 (gas) + HCl (gas)

(2) 2 HCl + Zn (liquid or vapor) → $ZnCl_2$ (particles - liquid at process bath temp.) + H_2

(3) 2 Zn (liquid or vapor) + O_2 (atmospheric) → 2 ZnO (particles, solid)

(4) 2 H_2 + O_2 (atmospheric) → $2H_2O$ (vapor)

As emitted particles cool (approaching 212°F) because of infiltrated air and radiation, further reactions could occur:

(5) $ZnCl_2$ (particles, liquid) → $ZnCl_2$ (particles, solid)

(6) NH_3 (gas) + HCl (gas) → NH_4Cl (particles, solid)

(7) $ZnCl_2$ (particles) + 2 HOH (from Reaction 4, atmosphere and/or fuel combustion products) $\rightleftarrows$ $Zn(OH)_2$ + 2 HCl. (Reaction takes place in particles because of deliquescence of $ZnCl_2$.)

(8) HCl (contained in particles from Reaction 7) + NH_3 (from Reaction 1) → NH_4Cl. (Reaction takes place in particles formed in Reaction 7. Resulting particles contain NH_4Cl, $ZnCl_2$, HOH, $Zn(OH)_2$, and HCl.)

(9) Zn (vapor) → Zn (particles, solid)

Pertaining to aluminum, further reactions could occur in the immediate region of bath surface:

(10) 2 Al (dissolved in bath) + 6 HCl (gas) → 2 $AlCl_3$ + $3H_2$

(11) 4 Al (dissolved in bath) + 3 O_2 (atmospheric) → 2 Al_2O_3 (particles, solid)

(12) 2 Al + 3 $ZnCl_2$ → 2 $AlCl_3$ (gas) + 3 Zn

In view of these reactions, it appears that the small amounts of aluminum likely to be contained in molten metal baths would not significantly influence the essential characteristics or quantities of emissions. Therefore, as a simplification of this analysis, aluminum is not considered further except to note that small quantities of aluminum compounds might be present in emissions.

Data presented in Chapter VI will show that cooling of emissions within the effluent stream, resulting from dilution with infiltrated air and radiation from ducts carrying effluent, reduces temperatures of effluents below the melting points of metallic zinc and $ZnCl_2$ and the sublimation (decomposition) point of NH_4Cl.

The generation of noncarbonaceous emissions from the process bath, as they exist in the effluent stream at the point of either being exhausted from the stack or entering a gas cleaning device, may then be summarized as follows:

A. $ZnCl_2$ particulate (solid) result from the following occurrences:

1. $ZnCl_2$ vapor is formed as $ZnCl_2$ flux vaporizes and as HCl (derived from NH_4Cl) reacts with elemental zinc vapor.

2. $ZnCl_2$ liquid particles are formed as $ZnCl_2$ vapor condenses, during cooling from the bath temperature range (800 to 1,100°F) to temperatures just above the melting point of $ZnCl_2$ (689°F).

3. $ZnCl_2$ solid particles are formed as the $ZnCl_2$ liquid particles solidify

on cooling to temperatures below the $ZnCl_2$ melting point (689°F).

B. ZnO particulate (solid) result from vaporization of metallic zinc followed by atmospheric oxidation of zinc vapor.

C. NH_4Cl particulate (solid) result from the following occurrences:

1. NH_3 and HCl gases are formed as NH_4Cl decomposes at temperatures above 662°F.

2. NH_4Cl solid particles are formed directly as NH_3 and HCl gases recombine on cooling to 662°F.

D. Particulate containing $ZnCl_2$, $Zn(OH)_2$, HCl, NH_4Cl, and HOH are formed as a result of the deliquescent adsorption of water by $ZnCl_2$ particles, as emissions cool to temperatures around 212°F and below. NH_3 gas (formed in Reaction 1) that does not recombine with gaseous HCl is probably adsorbed mostly into these particulates, forming NH_4Cl as in Reaction 8.

E. Metallic zinc particulate could be emitted through condensation of zinc vapor if a sufficiently reducing atmosphere in the furnace is obtained.

F. Particulate containing combinations of $ZnCl_2$, ZnO, and NH_4Cl are emitted as a result of mechanical entrainment of the residue-flux mixture into the effluent. $ZnCl_2$ in these particulates would be subject to the reactions with HOH and NH_3 noted previously.

G. NH_3 gas that does not recombine with gaseous HCl and is not adsorbed into partially-hyrolyzed particles, as described in D above, remains in the effluent gas stream as a gaseous emission.

For further consideration of the possible emission constituents several additional assumptions are believed justifiable:

1. Particles of $ZnCl_2$ and ZnO are formed generally separate from each other (not as particles containing mixtures of large percentage of both compounds), as $ZnCl_2$ vapor condenses to droplets that solidify on further cooling and as zinc vapor oxidizes directly to solid ZnO particles. This assumption is based on considerations of (1) the cyclic nature of the processes where flux or flux-containing residual scrap is manually applied at intervals, $ZnCl_2$ vaporization occuring in highest concentration immediately after flux application, and (2) the difference in vapor pressures of $ZnCl_2$ and elemental zinc tending to increase the ratio of $ZnCl_2$/ZnO emitted, at lower temperatures, the converse occuring at higher temperatures. Since ZnO particles would instantaneously result from zinc vapor oxidation those particles could act as nuclei on which $ZnCl_2$ vapor could condense. Some mixing might take place in this way.

2. Metallic zinc particles in the effluent are of negligible content because an oxidizing atmosphere in the effluent would normally be maintained by infiltrated air.

3. Gaseous NH_3 in the effluent is of negligible content because most NH_3 would either recombine with gaseous HCl or be adsorbed into $ZnCl_2$ particles as these particles adsorb moisture and hydrolyze to HCl and $Zn(OH)_2$.

The foregoing considerations therefore lead to the hypothesis that non-carbonaceous emissions resulting from melting, fluxing and working zinc-sweat process baths (at points in effluent streams where equilibrium mixtures are approached) consist mostly of combinations of particulate formed as shown in Items A, B, C, D, and F above (E and G omitted). These emissions may then be summarized as follows:

(1) $ZnCl_2$ particulate (solid)

(2) ZnO particulate (solid)

(3) NH_4Cl particulate (solid)

(4) Particulate containing $ZnCl_2$, $Zn(OH)_2$, HCl, NH_4Cl, and HOH (resulting from vaporization of molten zinc and flux, followed by oxidation, condensation, other chemical reactions and physical occurrences).

(5) Particulate containing combinations of $ZnCl_2$, ZnO, and NH_4Cl (resulting from entrainment from residue-flux mixture). Could include products of hydrolysis and other reactions of $ZnCl_2$.

Pertaining to particle size, it follows from the assumption listed as number one (above) that size of $ZnCl_2$ particles would depend on the time particles are maintained in the liquid state (above the melting point temperature of $ZnCl_2$), in which particle growth and agglomeration would most readily occur. High effluent flow rates and large volumes of infiltrated air impose rapid cooling and would therefore produce small particles. ZnO particles formed from oxidation of zinc vapor would be small because their formation in the solid phase would be instantaneous at the temperatures involved, with infinitesimal time available for particle growth.

FUEL COMBUSTION PRODUCTS

Mixing of air with fuel at burners is assumed satisfactory to effect complete combustion. It then follows that fuel combustion products consist essentially of CO_2, H_2O, and the residual N_2 that would remain after atmospheric O_2 is consumed in combustion. The content of nitrogen oxides and the possible presence of sulfur oxides and carbon monoxide in combustion products are not considered here. Those emissions do not appear significant to the problem area of this study. In any future work where it is desired to consider their affect on secondary zinc industrial emissions, results of studies specifically covering those gases should provide sufficient data. (Duprey, pp. 6-7)

TABLE V-1 - DATA PERTAINING TO MELTING, VAPORIZING, AND CONDENSATION OF ZINC-SWEAT PROCESS MATERIALS

Process Material Constituent	Melting Point		Boiling Point		Vapor Pressure at Pouring Temperature mm. Hg. *
	°C	°F	°C	°F	
Zinc	419**	786	907	1,665	< 1 to 15.2
NH_4Cl	dec. 350	dec. 662	---	-----	> 760
$ZnCl_2$	365	689	732	1,350	1 to 74
ZnO	>1800	> 3272	---	-----	0
Aluminum	660	1,220	2,056	3,734	< 1
$AlCl_3$ (or Al_2Cl_6)	---	-----	subl. 178	subl. 352	>760
Al_2O_3	2,000	3,630	2,210	4,010	0

* Pouring temperature of zinc sweat-process baths (APEM, p 293) : 800 to 1,100°F

** All data in this table is from Perry.

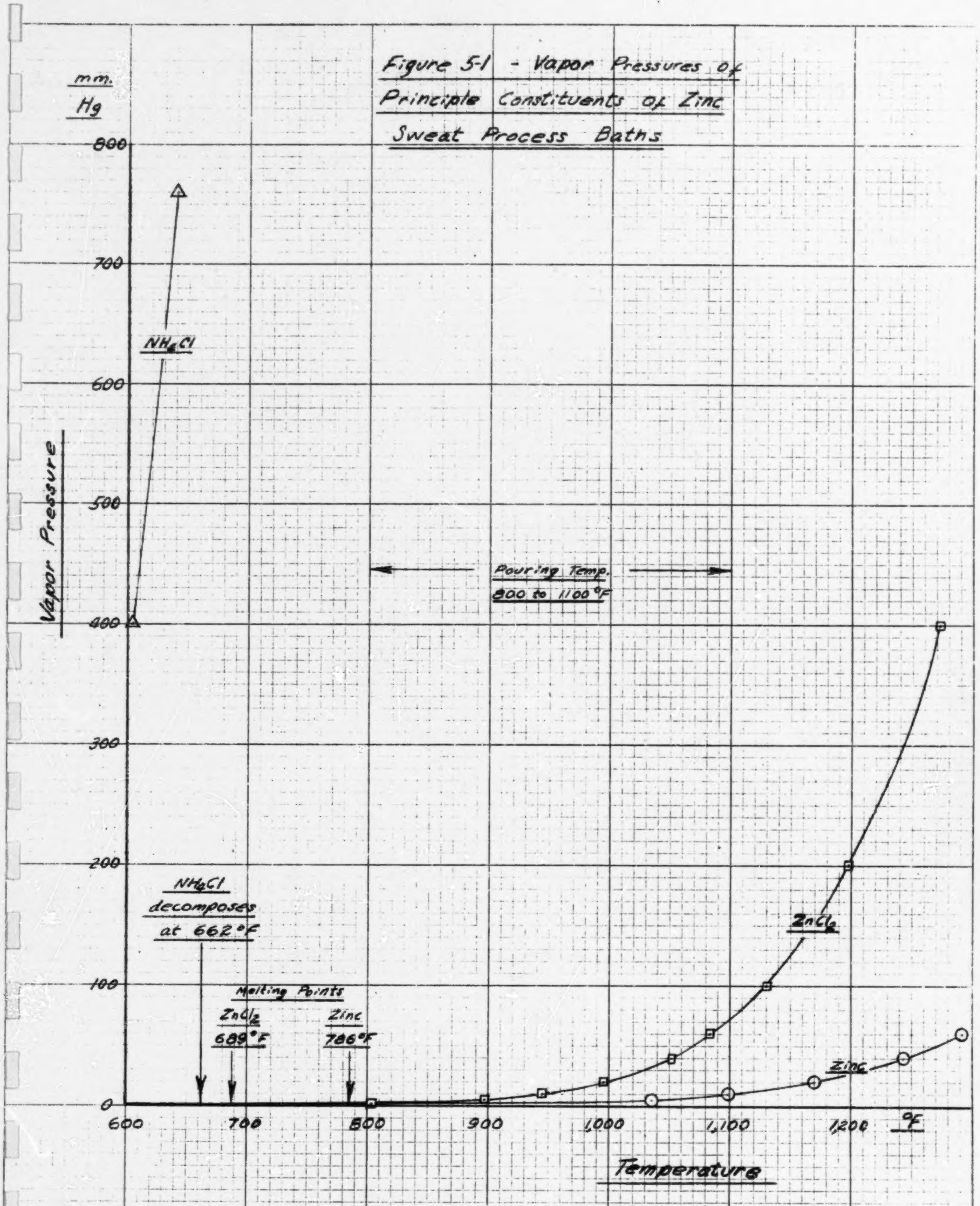

Figure 5-1 - Vapor Pressures of Principle Constituents of Zinc Sweat Process Baths

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KEUFFEL & ESSER CO. MADE IN U.S.A.

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Chapter VI

Emission Determinations and Correlation with Process Variables

SUMMARY

Processes of sweating zinc scrap materials are dealt with here. Data on processes and emissions were obtained and evaluated. Results are summarized in Table VI-1. The data were from phases of processing that included fluxing and did not include burning off large amounts of organic materials.

The data indicated that under the applied process conditions, mixtures of $ZnCl_2$ (hydrated) and ZnO make up most of the particulate emissions with carbonaceous particulates sometimes present in small amounts. Data also indicated that the gaseous part of effluents from kettle furnaces approaches atmospheric composition and that gases in reverberatory furnace effluents are mixtures of air with combustion products of fuel (usually natural gas). (Fuel combustion products from kettle furnaces are exhausted separately from metallurgical process effluents and are not considered here.)

It should be noted that during initial heating of charged metallic scrap, most of any organic materials in the charge would burn off, possibly resulting in carbonaceous particles making up most of the particulate emissions as well as emissions of gaseous compounds of carbon and other elements. As indicated above, no data were obtained on the highly carbonaceous emissions arising from this process phase, and results reported in Table VI-1 do not reflect such data. However, carbonaceous emissions in smaller amounts may occur after initial heating and burning-off because of many possible variations of process procedures and mixtures of scrap material charged. Such emissions are reflected in the results reported here. Chemical analysis of particulate emitted from one heat of residual scrap material indicated roughly 10% carbon compounds, the balance being mostly $ZnCl_2$ and ZnO. This carbonaceous content probably resulted from a quantity of metallic scrap containing organic substances in the charge.

The results reported here are believed reasonably representative of the range of zinc scrap material normally processed as stated. However, the data show emissions averaged over certain test periods. Also, these processes are cyclic; there are variations in operator judgement and in manually performed process operations. For these reasons, peak loadings might exceed those reported herein. Conversely, there are inactive periods during heats when emissions are insignificant. Further, the data sampling was small; there are data gaps; and certain conjectures were applied in arriving at results. These are detailed in the chapter text. Results should be useful in theoretical studies of emission control concepts, but more comprehensive data gathering and/or testing are needed to confirm results and fill data gaps.

EMISSION FACTORS - PARTICULATE

Emission factors were calculated from particulate emission rates of zinc-sweat processes as shown in Table VI-2. The emissions were from processing several different mixtures of residual and metallic scrap materials in kettle and reverberatory furnaces. Visual observations comparing emissions from kettle-sweat processing of several scrap material mixtures are shown in Table VI-3. (See REFERENCES TO DATA SOURCES, Chapter I.)

These emission factors and emission observations indicate correlations that may be summarized as higher emissions, and consequently higher emission factors, resulting from process variables noted as follows:

A. Metal bath temperature and amount of flux. Higher temperatures increase the vaporizing rate of both $ZnCl_2$ and Zn metal. Larger amounts of chloride flux also increase the amount of $ZnCl_2$ vaporized. These occurrences increase the amount of particulate emissions of $ZnCl_2$ and ZnO.

B. Residual scrap in charge. Dross derived from the tops of zinc processing baths requires relatively high temperatures and large amounts of flux to melt and separate zinc from Fe-Al compounds and metal oxides. Also, die-cast skimmings contain considerable residual flux. Thus, the necessary high processing temperatures and the large amounts of flux entailed in residual scrap processing cause high emission rates for the same reasons noted in Item A above.

C. Amounts of impurities in charges of metallic scrap. Impurities include organic materials, non-metallic residues (mainly metal oxides), and platings. Organic materials add directly to emissions where combustion is incomplete. Inorganic impurities require flux for removal (larger amounts of flux being needed where amounts of impurities are larger) with resulting increased chloride emissions.

Emission factors shown in Table VI-2 are higher for reverberatory furnaces than for kettle furnaces, if both furnaces process scrap materials that appear comparable. However, conclusions on the relative advantages of the two furnace types in reducing emissions cannot be drawn from these limited data. A full comparison would be considerably complex, and only a few comments will be made here. Where scrap charges contain carbonaceous substances, it appears that reverberatories could be advantageously operated to effect more complete combustion more readily than kettle processing. Probably the main cause of ZnO emissions from reverberatories is turbulence of hot gases contacting and vaporizing zinc during initial melting when there is little or no flux-residue cover over metal. However, in the same reverberatories, by applying flux after initial melting, with fuel combustion stopped or reduced, flux in the charge would not be subjected to as high turbulence of hot gas, and it appears that emission of chlorides could thereby be kept at minimum levels. Thus, whereas emission factors might be higher for reverberatories, chlorides (which are the most destructive constituent of emissions) are probably of lower concentration in reverberatory emissions as compared with emissions from kettle furnaces processing comparable charges. Reverberatory furnace design, as it affects heating of the charge by radiation vs. convection and hot gas velocity in charge region, probably has a considerable effect on emissions. As used in production, the two furnace types are each uniquely suited for certain types of work depending upon the type of charged scrap material.

In summary, the emission factors shown below (obtained from Table VI-2) appear representative of the types of processes and process materials listed:

Type of Furnace	Process Raw Material	Emission Factor lb./ton Process Material
Kettle-Sweat	Metallic Scrap: General Mixture	10.8
Kettle-Sweat	Residual Scrap: Mixed zinc die-cast dross & die-cast skimmings	24.5
Reverberatory-Sweat	Metallic Scrap: General Mixture	13.
Reverberatory-Sweat	Residual Scrap: Mixed die-cast dross & skimmings	32

EMISSION COMPOSITION - PARTICULATE

Particulate emission samples were collected from two separate zinc-sweat process runs and chemically analysed. Results are shown in the paragraphs that follow.

COMBINED EMISSIONS FROM ONE REVERBERATORY AND SEVERAL KETTLE FURNACES

Charges consisted of die-cast dross and/or die-cast skimmings. Some zinc metallic scrap, having carbonaceous content, might also have been included. Fluxing was by means of residual chloride flux and a small amount of NH_4Cl. Two samples of emitted particulates were obtained and analysed. Results of analyses were reported as follows.

All metal analyses were performed by atomic absorption spectroscopy. The samples were not completely soluble in any of several solvents tested including acids, aqua regia, organic solvents, and sodium carbonate fusion. Hot hydrochloric acid was found to dissolve 90% of the particulate. The insolubles appeared to be a carbonaceous material. Two working samples were taken from each container, dissolved in the acid, filtered and diluted to accommodate the linear range or the instrument. Results were as follows:

	Sample #1	Sample #2
NH_4^+	0.47%	0.36%
Cl^-	8.93%	8.32%
Zn	47.50%	44.50%
Al	1.43%	0.54%
Cu	0.04%	0.05%
Fe	0.40%	0.21%
Pb	0.14%	0.16%

(Listing continued on next page.)

	Sample #1	Sample #2
Cd	0.02%	0.03%
Mn	0.03%	0.01%
Cr	0.01%	0.004%
Totals	58.97%	54.18%

To determine the moisture content of the samples, specimens were weighed before and after oven drying, and results were obtained as shown below:

Drying Time & Temperature	**% Volatile**	
	Sample 1	**Sample 2**
4 hrs. at 120°C (248°F)	**3.0**	**7.1**
4 hrs. at 140°C (284°F)	**3.4**	**7.5**
Overnight (around 12 hrs) at 160°C (320°F)	**5.2**	**10.2**

During collection, the particulate contacted stainless steel parts of the collector, which underwent some corrosion. Infiltrated air entering exhaust ducts from the furnaces was of sufficient volume to reduce effluent temperature to 108°F. (Radiation from exhaust ducts probably accounts for a small part of the heat loss.) The collected particulates had been allowed to stand uncovered at least overnight before samples were extracted and sealed in containers to await analyses. The samples had the appearance of light gray, low-density powder.

Because of atmospheric moisture in the large amount of infiltrated air the following effects probably occurred. The emitted $ZnCl_2$ was fully hydrated to $ZnCl_2 \cdot 4H_2O$ (Mathewson p. 661) while particulates were still in the effluent gas stream. Further moisture adsorption by deliquescence of the hydrated $ZnCl_2$ occurred during overnight atmospheric exposure of the collected particulate. Any other metal chlorides present, particularly $AlCl_3$ and

$MgCl_2$, underwent similar moisture adsorption. The effect of moisture adsorption was probably accentuated by the extreme porosity of the collected mass caused by the presence of extremely small acicular ZnO particles (APEM pp. 271-73).

Besides those metals included in the analyses listed above, other metals that could be present in small quantities (derived from alloys processed, melting vessels, corrosion of stainless steel, and impurities) include Mg, Sn, Ni, Si, Ca, and Na.

To obtain an approximate, complete analysis showing compounds that make up particulate emissions, the following assumptions that are based on above considerations and believed to approximate actuality are applied:

A. All NH_4^+ is combined as NH_4Cl.

B. The balance of Cl^-, not combined as NH_4Cl, is combined as $ZnCl_2$. (Actually, Cl^- probably combines preferentially with Al and Mg. However, quantities of these metals likely to be contained in process baths are considered small enough to permit this simplification.)

C. $ZnCl_2$ is present as the hydrate $ZnCl_2 \cdot 4H_2O$. (In the tabulations that follow, amounts of this compound are shown as equivalent anhydrous $ZnCl_2$, with water of hydration itemized separately.)

D. 10% of the particulate samples are carbonaceous material (indicated in test report as noted above).

E. All other compounds composing particulates are metal oxides, aluminum being present as Al_2O_3, iron as Fe_2O_3, and lead as PbO.

F. Metals other than Zn, Al, Fe, and Pb in collected particulates total 1%, and their oxides total 2% of sample weight.

G. Moisture adsorbed by deliquescence (in excess of water of hydration) equals the percent volatile determined by drying specimens overnight at 320°F, shown above.

Compositions of samples are then calculated as shown in Calculation Sheets 1 and 2 and are tabulated as follows:

Component	**Sample 1 (%)**	**Sample 2 (%)**
$ZnCl_2$	15.3	14.5
ZnO	50.0	46.9
NH_4Cl	1.4	1.1
Al_2O_3	2.7	1.0
Fe_2O_3	.6	.3
PbO	.2	.2
H_2O (in $ZnCl_2 \cdot 4H_2O$)	8.1	7.7
Oxides of Mg, Sn, Ni, Si, Ca, Na	2.0	2.0
Carbonaceous Material	10.0	10.0
Moisture (deliquescent)	5.2	10.2
Total	95.5%	93.9%

COMBINED EMISSIONS FROM SEVERAL KETTLE FURNACES

Emissions were from charges of mixed die-cast dross and skimmings. Fluxing was by means of residual chloride flux. Effluent particulates were sampled in the header, which connects furnace exhaust ducts to the stack, and analysed. Sampling was by means of extraction thimbles. Results of analysis were as follows:

17.7% chlorine as chlorides (Cl^-)

48.3% free and combined zinc (total Zn)

No additional data were obtained on composition of particulates. The test report noted that emissions were sampled at times when melt kettles were being skimmed to obtain peak loadings. Effluent was exhausted by means of natural draft and consisted principally of air and particulate emissions. Analytical methods were not detailed in the test report, but it is presumed that standard techniques were applied with samples sealed in containers immediately after collection to await chemical analysis.

To obtain an approximation of amounts of principle compounds in sampled particulates, it is assumed that (A) all Cl^- is combined as $ZnCl_2$; (B) all $ZnCl_2$ is present as the hydrate $ZnCl_2 \cdot 4H_2O$; and (C) all Zn other than that in $ZnCl_2$ is present as ZnO. Calulations are then made as shown in Calculation Sheet 3. Results obtained are as follows:

Compound	Amount (%)
$ZnCl_2$	33.8
ZnO	40.0
H_2O (in $ZnCl_2 \cdot 4H_2O$)	18.0
Total	91.8%

The balance (8.2%) is probably made up of about 4% other metal oxides in quantities approximating those shown for the previously discussed samples and about 4% water of deliquescence and/or carbonaceous particles.

Comparing analyses of emissions from reverberatory and kettle furnace combinations (discussed first above) with those of kettle furnace emissions tends to confirm that percentages of $ZnCl_2$ in reverberatory emissions are likely to be lower (and ZnO percentages higher) than in kettle furnace emissions (as suggested by considerations noted in discussion of EMISSION FACTORS Above).

The emissions studied here are from processes where amounts of chloride flux, expressed as percentages of the total charge, approach the maximum for the range of zinc scrap materials that are normally sweat-processed. It appears therefore that percentages of chlorides in the resulting emissions would also approach the maximum. Conversely, percentages of ZnO would approach the minimum. The opposite trend of emission composition would be anticipated for processing clean, unplated castings where little or no chloride flux is contained in the charge. It then follows (considering data shown above) that the range of composition of particulate emissions from zinc-sweat processes may be summarized by the following approximations:

Type of Scrap Material Making Up Charge	Constituents of Particulate Emissions	
	$ZnCl_2$	ZnO
Clean, unplated Zn castings	Approaches 0%	Approaches 100%
Residual Zn scrap	34%	40%

That is, $ZnCl_2$ would range from 0 to around 34% and ZnO from around 40 to 100% of particulates emitted from all zinc-sweat processes, the actual amounts depending upon type of scrap processed and amount of flux applied.

It should be noted, however, that zinc-sweat processing is highly cyclic. The ranges above are representative of emissions averaged over periods of time that include fluxing. Therefore, peak loadings may exceed those ranges.

It should also be noted that the above ranges, being applicable to phases of processing that include fluxing, are based on the supposition that any carbonaceous particulates present would be of relatively small amount. Undoubtedly, where charges contain large amounts of organic materials, preponderances of carbonaceous particulate emissions result. It appears that such highly concentrated carbonaceous emissions would take place mainly during initial heating of charged material and that flux would be added after most organic materials are burned off.

PARTICLE SIZE AND CHARACTERISTICS

EMISSIONS FROM CHARGES OF MIXED RESIDUAL ZINC-SCRAP MATERIAL - KETTLE-SWEAT PROCESSED.

A particulate sample was obtained from the effluent during a process run using a standard impinger containing alcohol. Fluxing was by means of residual chloride flux in charged die-cast skimmings. Particles were measured by means not noted in the test report but presumed to be an optical microscope. Sizes were reported by percent distribution as

60% - 0 to 10 microns
17% - 11 to 20 microns
23% - Larger than 20 microns

During this test, stack gas was analysed. Results were reported as

CO - 0.01% by volume
CO_2 - none found
O_2 - 19.7% by volume

This analysis indicates little or no carbonaceous substance in the charge during the test and probably no carbonaceous particles in the sampled particulates. No chemical analysis of particulates was obtained. However, analysis of particulates from similar processing (covered under EMISSION COMPOSITION) indicated those considered here would be mostly a mixture of $ZnCl_2$ and ZnO with analysis about the same (around 17.7% Cl^- and 48.3% Zn; or 33.8% $ZnCl_2$, 40% ZnO, and 18% water of hydration).

EMISSIONS FROM CHARGES OF MIXED METALLIC ZINC-SCRAP MATERIAL - KETTLE-SWEAT PROCESSED

Particulate samples were obtained from the effluent during a process run using a stainless steel nozzle-thimble holder connected through a stainless steel probe to a Greenberg-Smith impinger (500ml). Fluxing was by means of chloride flux added to the charge. Most particulates were found in thimbles, very little in impingers. Particles collected in thimbles were measured using a conventional microscope (oil immersion). Three determinations were made of geometric mean values (50% less than size). Results were reported as follows:

1.1 microns
1.3 "
1.6 "

Many agglomerates were observed in the microscope field that were not included in the particle size determination.

The report stated that qualitative and semi-quantitative tests of sampled particles indicated significant amounts of Zn, Mg, and Na, with traces of Al, Cu, and Fe. It did not mention any indication of carbon content in emissions. It was noted that the furnace operator was instructed to flux the furnace at least once during the sampling period, which indicates that most of any carbonaceous material in the charge was probably burned off before particles were sampled.

As in the previously discussed sample, the particulates considered here are probably mostly a mixture of $ZnCl_2$ and ZnO but with a lower percentage of Cl^- and a higher percentage of Zn because of the difference in the type of charge, relatively less flux usually being contained in metallic scrap charges than in residual scrap charges (See Tables VI-2 and VI-3).

ZINC OXIDE PARTICULATE

To study the ZnO-particulate constituent of zinc-sweat process emissions, it is useful to consider emissions from secondary processing of copper-zinc (brass) alloys that involve "blowing" of alloy baths with compressed air to remove impurities, such as iron, by oxidation. Other alloy metals that may be present are lead and tin (APEM p. 271). Of the alloy metals composing the process bath, zinc has the lowest boiling point at 1663°F as compared to 3160, 4120, and 4703°F for lead, tin, and copper, respectively. Fluxes for brass processing are generally inert materials used in small quantities to cover the bath, prevent oxidation at the bath surface, and mix with metal oxides that are formed. Resulting emissions contain as high as 96% ZnO, which results from vaporizing followed by oxidation of Zn. Thus ZnO particulate is generated during brass blowing through the same mechanism as in zinc-sweat processing - vaporizing followed by atmospheric oxidation. Other particulate emitted from brass blowing would include oxides of lead and tin and flux particles, mechanically entrained in effluent gas, that would not have deliquescent or fusing properties similar to $ZnCl_2$. Under these conditions, characteristics of ZnO particles in effluents are less obscured and interfered with by other effluent constituents than is the case in zinc-sweat emissions. Therefore ZnO particulate as emitted from brass blowing may be studied under more ideal conditions.

Particle sizes of ZnO fumes are reported as 0.03 to 0.3 micron in APEM (pp. 271-3). The same reference shows electron photomicrographs of fume from a zinc smelter and a yellow brass furnace. These figures show star shapes of ZnO particles with thin rod-like formations radiating from the nuclei. A loose agglomeration of these particles is shown in Figure 185 (APEM).

Particle size measurements of emissions sampled during the blowing operation of a secondary brass-process heat showed a geometric mean size of 1.1 microns, measured by optical microscopy. Chemical analysis of particles sampled showed 46% Zn, 8% Pb, and 5% Sn.

The above data indicate that as initially formed, ZnO particles are of sub-micron size and that these particles form mechanically attached agglomerates (not bonded by liquification of fusion). These agglomerates appear as particles of approximately one micron in normal optical microscopic observation and measurement.

ZINC CHLORIDE PARTICULATE

Data on effluent streams having particulates with primarily $ZnCl_2$ content were not obtained during this study. An estimate of $ZnCl_2$ particle size is arrived at below by applying data presented in previous paragraphs involving particulate $ZnCl_2$ and ZnO emitted in mixtures.

Data cited previously showed that particulates emitted from a kettle-processed, chloride-fluxed, zinc-scrap charge (which would have consisted mainly of $ZnCl_2$ and ZnO particles) were of around one micron, which was about the same size indicated for ZnO particles emitted from brass processing and zinc smelting. It follows from this comparison of sizes between mixed-$ZnCl_2$-and-ZnO particles and ZnO particles (the latter being in approximate isolation) - all being around one micron - that size of emitted $ZnCl_2$ particles must also approximate one micron. This applies to emissions from kettle-sweat processing. Average particulate $ZnCl_2$ emitted from reverberatory sweat processing might be somewhat larger because combustion products in the effluent could cause slower cooling during part of the processing, with $ZnCl_2$ particles being maintained longer in the liquid phase, allowing particle growth. However, this effect would tend to be balanced by higher exhaust flow rates required to remove fuel combustion products from reverberatories.

EFFLUENT TEMPERATURE, FLOW RATES, AND GAS COMPOSITION

In the kettle sweat processes studied in this investigation, fuel combustion products were exhausted separately from process bath emissions. Melting kettles (or kettle-sweat furnaces) were enclosed in hoods with doors that were opened during a considerable part of process time to permit charging, fluxing, sampling, skimming, and removal of unmeltables and through which air could infiltrate into the effluent.

Reverberatory furnaces had openings for charging, fluxing, skimming, and removal of unmeltables. Hoods at such openings were used during process operations that involved emissions. The effluent was composed of flue gas containing bath emissions, fuel combustion products, and infiltrated air as well as emissions and air collected at hoods.

In the following paragraphs, temperatures, flow rates, and gas composition of process exhaust effluents, resulting from the occurrences mentioned above, are shown and discussed.

EFFLUENT TEMPERATURE

Temperatures of all effluent streams from zinc-sweat processes that were obtained during this study are shown with related data as follows:

Furnace Type	Draft Type	Process Scrap-Mat'l. Type	Effluent Flow Rate SCFM	Effluent Temp. °F	
Kettle	Induced	Residual	1,850	176	Avge. 148
Kettle	Induced	Residual	395	118	
Kettle	Induced	Residual	2,180 ACFM	147	
Kettle	Natural	Metallic	3,960 *	195	
Kettle	Natural	Metallic	4,540 *	105	

Furnace Type	Draft Type	Process Scrap-Mat'l. Type	Effluent Flow Rate SCFM	Effluent Temp. °F
Reverberatory (APEM p. 307)	Induced	Metallic	7,680	190
Reverb.-Kettle Combination	Induced	Residual	13,400	108

* Concurrent processing in same plant

All of the above temperature measurements were made in stacks or in headers leading directly to stacks. There had been no treatment of effluent before temperature measurement, so the only cooling of effluent had been by air infiltrated at the furnaces and by radiation from exhaust ducts.

EFFLUENT FLOW RATES

Exhaust effluent flow rates of zinc-sweat process runs, involving kettle and reverberatory furnaces, are tabulated in Table VI-4. From these flow rates, effluent flow factors (defined here as cubic feet of exhaust effluent flow per ton of scrap material processed, i.e. process weight) were calculated and are shown in the table. In all of the tabulated processes, effluents were exhausted by induced drafts. It is assumed that flow rates induced were those required to efficiently exhaust emissions that result from the process conditions shown in the table.

Effluent flow factors provide a means of relating process weight rates with flow rates required to exhaust resulting effluents. Those shown below, obtained from Table VI-4, appear representative of the types of processes and materials listed. However, it should be noted that they were derived from a small sampling of data and are therefore subject to confirmation through more comprehensive data gathering and analysis.

Furnace Type	Process Scrap-Mat'l. Type	Effluent Flow Factor - Cu. Ft. Exh. Effluent Per Ton Process Mat'l.	
Kettle	Residual	222,000	Avge. 200,000
Kettle	Metallic	185,000	
Reverberatory	Residual	840,000	
Reverberatory	Metallic	443,000	

These values indicate that higher effluent flow rates, and consequently higher effluent flow factors, result from processing residual scrap as compared with metaliic scrap and from reverberatory processing as compared with kettle processing. Higher bath temperatures involved with residual scrap processing and reverberatory furnace applications (as well as the need to exhaust fuel combustion products from reverberatories) probably account for this trend.

EFFLUENT GAS COMPOSITION

Kettle Furnaces

Stack gas analysis, which was available for one kettle process run (Column 7, Table VI-4), indicated only a trace of carbon oxides and a percentage of oxygen approaching the usual atmospheric concentration (19.6% O_2 in stack gas compared with 21.0% O_2 in normal dry air). This O_2 concentration and data shown above on the temperature of effluent from kettle-sweat processes (in most cases, considerably less than 200°F) tend to confirm the previously presented hypothesis that where charge is free of carbonaceous substances, the gaseous portion of kettle-sweat effluents consists essentially of air. The 1.4% difference between the O_2 in stack gas and the O_2 in normal dry air is probably due to particulates and moisture in the stack gas. Although some effluent cooling would result from exhaust duct radiation, it seems that the consistently low effluent temperatures would result mainly from air infiltration.

Indications that free NH_3 might be present in effluents were not noted in any test reports obtained during this investigation. Also, there was no mention of the presence of NH_3 in discussions with company representatives, and indications of emitted NH_3 were not noticed during visits at plants. It appears most likely that any free NH_3, generated from reactions involving NH_4Cl flux in zinc-sweat processing, is adsorbed with moisture into $ZnCl_2$ and other metal chloride fumes. Such adsorption appears to occur in emissions from galvanizing processes where "fumes escaping contain an excess of ammonia" (APEM p. 402) and where fume analysis shows small percentages of NH_3 (APEM p. 405).

Reverberatory Furnaces

Chemical analyses of the gaseous constituents of exhaust effluent from reverberatory furnaces were not available during this investigation. Analyses of such gas mixtures were estimated for one reverberatory furnace by considering the known combustion rate of the natural gas fuel, applying the following assumptions, and calculating results shown below and in Columns 8-11, Table VI-4.

Assumptions:

A. Air entering the furnace during burner operation is 20% in excess of the theoretical natural gas combustion requirement.

B. Additional infiltrated air entering the effluent during burner-off time equals 10% of total effluent.

C. All moisture in the air entering the effluent is adsorbed by particulate metal chlorides. Air entering the effluent is therefore considered dry.

D. The volume of emitted particulates (including adsorbed moisture) is small enough to be neglected. Total effluent flow rate is therefore considered equal to effluent gas flow rate.

E. The charge is free of carbon compounds or other combustible or volatile, non-metal compounds that would add to gaseous emissions.

Then, during any processing period (designated here as a run), the following equations are applicable:

A. Effluent gas, during burner-on time = natural gas combustion products including 20% excess air. (Let this combustion-product-and-air mixture be designated "C.P.")

B. Effluent gas, during burner-off time = dry air.

C. Effluent gas, for total run = C.P. that occurs during fraction of run time burners are operated + additional infiltrated air entering effluent during burner-off time. (Let fraction of run time burners are operated be designated "F".)

D. Total effluent gas flow rate = (flow rate of C.P., during burner-on time) times (F) + (.10) times (total effluent gas flow rate).

("Total effluent gas flow rate" expresses an average value for the total run including burner-on time and burner-off time.)

Where:

Total effluent gas flow rate = total effluent flow rate = 7000 cu. ft/min. (Col. 4, Table VI-4)

Flow rate of C.P. during burner-on time = 13.5x1,600 = 21,600 cu. ft/min. (Col. 8, Table VI-4; and APEM p. 882)

Then, substituting in equation D:

$$7000 = 21{,}600 \times F - .10 \times 7000$$

$$F = \frac{7000 - .10 \times 7000}{21{,}600} = .29 \text{ or } 29\%$$

That is, 29% of the total effluent gas has the composition of C.P.

Determination may then be made of effluent gas composition during burner-on time and of percentages of C.P. (constituent) gases in the total effluent, as follows:

C.P. Gases (See APEM p. 882)	Vol. of C.P. Gases from 1 cu. ft. Natural Gas	% C.P. Gases in Effluent During Burner-on time	% C.P. Gases in Total Effluent
CO_2	1.13 Cu. Ft.	$\frac{1.13}{13.52} = 8.4\%$	8.4x.29 = 2.4%
H_2O	2.08	$\frac{2.08}{13.52} = 15.4\%$	15.4x.29 = 4.5%
N_2	9.87	$\frac{9.87}{13.52} = 72.9\%$	72.9x.29 = 21.2%
O_2	0.44	$\frac{0.44}{13.52} = 3.3\%$	3.3x.29 = .9%
Total	13.52 Cu. Ft.	100%	

The remaining 71% of the total effluent has the composition of dry air.

Effluent gas during burner-off time has the composition of dry air, which is listed below. Also listed are percentages of dry air (constituent) gases in total effluents, calculated as shown:

Dry-Air Gases	% Dry-Air Gases in Effluent During Burner-off Time	% Dry-Air Gases in Total Effluent
N_2	78%	78x.71 = 55.4%
O_2	21%	21x.71 = 14.9%
Other	1%	1x.71 = .7%
Total	100%	

Combining the above, an estimated analysis of total effluent gas (stack gas) from a reverberatory-sweat process run is obtained as follows:

% CO_2	% H_2O	% N_2	% O_2	% Other
2.4	4.5	21.2	.9	-
-	-	55.4	14.9	.7
2.4	4.5	76.6	15.8	.7

Sum of above equals 100%

It should be noted that in arriving at the above approximation, combustion characteristics of natural gas shown in Table D7, p. 882, of the APEM are applied. The values in Table D7 do not include nitrogen oxides and the probably-insignificant amounts of CO and sulfur oxides contained in natural gas combustion products (Duprey, p. 6). This simplification is believed justified in view of the problem area of this study. A more rigorous treatment would be needed in evaluating total secondary zinc industrial emissions.

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Table VI-1 - Summary of Results of Process and Emission Data Evaluation

Emission Properties and Related Process Variables	Type of Process Furnace and Zinc-Scrap Material Charged					
	Melt Kettle (Sweat Process)			Reverberatory (Sweat Process)		
	Metallic, Clean	Metallic, General*	Residual**	Metallic, Clean	Metallic, General*	Residual**
Emission Rates - Particulate -lb/hr.	Approaches 0	4 to 64 for various furnace combinations		Approaches 0	13.5 for 1 furnace	20 for 1 furnace
Emission Factors - Particulate, lb/ton Process Mat'l	Approaches 0	10.8	24.5	Approaches 0	13	32
% Chlorine (Cl^-) in charge, derived from flux.	Approaches 0	to 0.15%	to 3.0%	Approaches 0	No data	to 3.0%
Composition of Emitted Particulates { %$ZnCl_2$ %ZnO	Approaches 0 Approaches 100%	0 to 34% 100 to 40%	34% 40%	Approaches 0 Approaches 100%	15% or less 50% or more	
Particle Size of Emitted Particulates { $ZnCl_2$	around 1 micron			No data - Probably around 1 micron and less		
{ ZnO		0.03 to 0.3-micron particles; 1-micron agglomerates				
Effluent (Exhaust Gas) Temperature - °F	105 to 195 °F for various furnace combinations.			No data	190 °F for 1 furnace	No data
Effluent Flow Rates - Approximate SCFM	2,000 to 16,000 for various furnace combinations			No data	7,680 for 1 furnace	7,000 for 1 furnace
Effluent Flow Factors - cu. ft. Exhaust Effluent per Ton of Process Material.	No data	Around 200,000		No data	400,000 to 800,000	
Effluent Gas Composition:	(For charged zinc scrap materials that contain no organic substances.)					
Burners on	Approximates Atmospheric Air Around 78% N_2 Around 21% O_2			No data		8.4% CO_2 15.4% H_2O 72.9% N_2 3.3% O_2
Burners Off	Air (Same as above)			No data - would approximate Air		78.0% N_2 21.0% O_2
Total Run (Average)	Air (Same as above)			No data		2.4% CO_2 4.5% H_2O 76.0% N_2 15.8% O_2

**"Residual" zinc-scrap materials consist of drosses and skimmings.

* "General" metallic-zinc scrap materials are meant to include mixtures of all types of metallic scrap (without excessive amounts of impurities), the resulting emission characteristics approximating the average for metallic scrap.

Table VI-2 - Determination of Emission Factors of Secondary Zinc-Sweat Processes

Type of Furnace Used During Test	1 Type of Scrap Material Processed	2 Type of Flux Applied	3 Process Weight Rate lb scrap/hr per furnace	4 Process Weight Rate lb flux/hr per furnace (Approximations)	5 Particulate Emission Rate lb/hr per all furnaces	6 Particulate Emission Rate lb/hr per furnace (Column 5 ÷ No. of furnaces)	7 Emission Factor lb particulate per ton process material (Col. 6 ÷ Col. 3)	8 Sampling Method	9 Bath Temperature °F	10 11 12 Notes
Melting Kettle (6)	Die-cast dross and skimmings mixtures	Residual flux in skimmings.	500 (¼ ton)	10*	63.7 47.6	10.6 7.94	42 32	Extraction thimbles	900	* Fluxing is by means of residual flux. These figures were calculated assuming ½ charge is of die-cast skimmings, containing 4% $ZnCl_2$, so that total charge would contain 2% by weight of $ZnCl_2$. (Reference: Mathewson p. 315)
Melting Kettle (1)	same	same	800 (.4 ton)	16*	4.06 7.23	4.06 7.23	10 18 } 24.5 Ave.	Std. Impinger containing alcohol		
Melting Kettle (2)	same	same	500 (¼ ton)	10*	18.3 3.78	9.2 1.89	37 8	Greenberg-Smith impinger	900	
Reverberatory (1)	Die-cast dross	NH_4Cl (Residual flux might also be present)	1000 (½ ton)	1-lb NH_4Cl/hr + unknown residual flux	16**	16	32	ASTM PT. C21	1000	** Effluent of this reverberatory was combined with that of several kettle furnaces, processing mixed die-cast dross and skimmings, and the combined effluent stream sampled. Results shown here were calculated by applying emission factor 24.5 to determine rate of particulate emission from kettles, then subtracting that rate from the total particulate emission rate (determined by sampling.)
Melting Kettle (7)	Unplated and plated castings and fabricating scrap.	$ZnCl_2$	1,290 (.65 ton)	0.66	Unknown	Unknown	10.8 (Assumed. See note in last item below.)		900	
Reverberatory (1) 5 ft. 9 in. W x 6 ft. 4 in. L x 4 ft. H (Reference APEM p. 307)	Zinc castings	Unknown (Probably $ZnCl_2$ or NH_4Cl)	2,080 (1.04 ton)	Unknown (Probably small amount)	13.5	13.5	13	Unknown	Unknown	
Particulate emission factor for "Zinc sweating furnace" shown in Table 24, Compilation of Air Pollution Emission Factors (PHS No. 999-AP-42) 1968.	Unknown	Unknown	———	———	———	———	10.8	———	———	

The type of process furnace and scrap material processed are not shown in the reference. The reference emission factor (10.8) indicates a low to medium emission level, by comparison with the other emission factors shown above. Table VI-3 indicates that such emission levels are characteristic of kettle-sweat processing of general mixtures of metallic scrap (not containing large amounts of impurities). It is therefore believed that the factor (10.8) can be realistically applied to the above melting-kettle processing of "Unplated and plated castings and fabricating scrap."

Table VI-3 - Visual Comparison of Emissions Resulting From Various Process Materials - Secondary Zinc-Sweat Processes

Type of Furnace	Type of Scrap Material Processed	Type of Flux Applied	Process Weight Rate		Observations of Emissions	Bath Temperature (Approximate) °F
			lb scrap/hr per furnace	lb flux/hr per furnace (Estimations)		
Melting Kettle (1)	Clean zinc scrap - unplated castings, off-grade ingots.	$ZnCl_2$	2000	.17	Practically no emissions	850
Melting Kettle (1)	"New" and/or "old zinc". Mainly unplated zinc castings. Relatively clean, with small amount of organic material.	$ZnCl_2$	2100	.2 to 1	Low level of emissions. Includes small amount of fly ash.	850
Melting Kettle (1)	Mixtures of plated Zinc castings and contaminated zinc die-cast scrap.	$ZnCl_2$	1400	1.7 to 2.5	Medium level of emissions	850
Melting Kettle (1)	Zinc die-cast dross	$ZnCl_2$	1700	5 (0.3% of charge wt.) (0.15% Cl-)	Highest level of emissions of the materials shown here	1000

Table VI - 4 (page 1 of 2) - Determination of Exhaust Effluent Flow Volumes as Functions of Process Weight***; and Stack Gas Analysis

Type of Furnace Used During Test	1 Type of Scrap Material Processed	2 Process Wt. Rate lb scrap/hr per furnace	3 Exhaust Effluent* Flow Rate cu. ft./min. from all furnaces	4 Exhaust Effluent* Flow Rate cu.ft./min. per furnace (Col. 3 ÷ No. of furnaces)	5 Exhaust Effluent Flow (cu. ft.) per Ton of Process Mat'l. (Col. 4 ÷ Col. 2) (Effluent Flow Factor)	6 Exhaust Effluent Temp. ^{o}F
Melting Kettle (2)	Die-cast dross and skimmings mixtures.	500 (¼ ton)	2,220 @ 176°F 1,850 @ 70°F	925	222,000 200,000 Avge.	176
Melting Kettle (8)	Unplated and plated castings & fabricating scrap.	.65 ton	16,000 @ 70°F (std. temperature assumed)	2,000	185,000	unknown
Reverberatory (1)	Die-cast dross	1,000 (½ ton)	7,000 ** @ 70°F	7,000	840,000	108 (temp. of combined stream from reverb. & kettles)
Reverberatory (1) 5 ft. 9 in. W x 6 ft. 4 in. L x 4 ft. H (Reference APEM p.307)	Zinc castings	2,080 (1.04 ton)	7,680 @ 70°F	7,680	443,000	190

* See definition of effluent (exhaust effluent) in Chapter V.

** Effluent from this reverberatory was combined with that of several kettle furnaces, processing mixed die-cast dross and skimmings; and flow rate of the combined (total) effluent stream was measured by pitot traverse. Results shown here were calculated by applying the effluent-flow factor 200,000 to determine effluent flow rate from the kettles, then subtracting that rate from the total measured rate to obtain the rate shown for the reverberatory.

*** This function is defined as effluent flow factor as illustrated in Column 5.

Table VI - 4 (page 2 of 2)

Type of Furnace Used During Test	7 Stack Gas Analysis (Chemical analysis of gas sample) % by Volume	8 Natural Gas Combustion Rate During Burner Operation cu.ft./min.	9 Products-of-Combustion Flow Rate During Burner Operation (20% excess air assumed) cu.ft./min. (13.5 x Col. 8)	10 Fraction of Run Time Burners are Operated (10% Infiltrated air assumed) (Col. 4 - .10 x Col. 4) ÷ Col. 9	11 Stack Gas Analysis (Calculated, based on assumptions of Columns 9 and 10) % by Volume (Avge. for total run)	12 Stack Gas Analysis (Calculated - See text Chapter 6) % by Vol. (During burner-on time)	13 Stack Gas Analysis (Calculated - See text Chapter 6) % by Vol. (During burner-off time)
Melting Kettle (2)	CO .01 CO_2 - none O_2 - 19.6						
Melting Kettle (8)							
Reverberatory (1)		1,600	21,600	0.29 (29%)	CO_2 - 2.4 H_2O - 4.5 N_2 -76.6 O_2 -15.8 Other - .7	CO_2 - 8.4 H_2O - 15.4 N_2 - 72.9 O_2 - 3.3	N_2 - 78 O_2 - 21 Other - 1
Reverberatory (1) 5 ft. 9 in. W x 6 ft. 4 in. L x 4 ft. H (Reference APEM p. 307)							

Chapter VII

Process Modelling

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ZINC SWEAT PROCESS MODEL UNITS VII-1 (pages 1,2)

Chapter VII

Process Modelling

DEFINITION OF PROCESS MODEL UNITS

Process model units, defined by characteristics of secondary zinc production processes and resulting emissions, are formulated here. The purpose of these units is to provide a basis for studies of emission control concepts.

Five model zinc-sweat process units were formulated and are shown in Table VII-1. Each of these units represents an application of one furnace and is defined, basically, by the type of furnace, types of materials composing the charge, and process weight rate. (For brevity in the following discussion, the model units will be referred to simply as models.)

The models are defined in further detail by values, shown in Table VII-1, representing further process and emission data. These values, as filled in for each model, were derived through consideration of data from several actual process runs (covered in previous chapters) where process conditions appeared reasonably comparable, and through theoretical considerations. These values are believed to reasonably approximate data that would be obtained from processes conducted under the stated conditions. Key considerations in deriving the tabulated values for the models are shown in Appendix A.

COMPOSITE EMISSIONS

It should be noted that during a process heat, carbonaceous emission may partly or entirely precede non-carbonaceous emissions (See Chapter V). Therefore, the values shown in Table VII-1 pertaining to emissions should be regarded as applying to composite emissions taking place over periods of time involving melting, fluxing, and working process baths when both types of emissions might occur.

PROCESS CONDITIONS NOT INCLUDED IN MODELS

Several process conditions that were not considered in formulating the models are listed below with reasons for emission.

MELTING CLEAN ZINC CASTINGS

Clean zinc scrap may be melted in all types of zinc sweating furnaces without generating significant emissions. Emission control equipment is not required under this condition. Therefore processing clean scrap is not included in process modelling.

ROTARY SWEAT PROCESSING OF CONTAMINATED DIE CAST SCRAP

Findings of this study indicated that charges to rotary-sweat furnaces usually do not contain chloride flux and that emissions from those furnaces are usually satisfactorily controlled by afterburners. Therefore, there was no apparent need for a rotary furnace process model to study chloride emissions. Also, no data were available during this study on rotary furnace emissions. Findings were based on experience of plant operators.

OCCURRENCE OF A REDUCING ATMOSPHERE IN REVERBERATORY FURNACES

If the atmosphere in the sweating chamber of a reverberatory furnace were not sufficiently oxidizing because of insufficient infiltrated air, combustible effluent mixtures including carbonaceous particulates, gases such as CO, and metallic zinc particles could result. This might occur if the furnace were closed during melting of the charge; however, no indications of this occurrence were found during this study. Also, because of process operations conducted on furnace charges, there would nearly always be sufficient infiltrated air to prevent a reducing atmosphere. (The low effluent temperature shown for reverberatory furnaces on page VI-16 is an indication of such high dilution of reverberatory furnace effluents with infiltrated air.) Since the process condition cited here seems unlikely, it was not considered in process modelling. This condition is noted because it poses the possibility of a fire hazard, which, though remote, should not be overlooked.

MAKING UP PLANT PROCESS MODELS FROM PROCESS MODEL UNITS

To make up hypothetical plant process models for the purpose of studying emissions and emission control concepts, the model units defined in Table VII-1 may be combined. For example, the following combinations might be made for such study:

12 Model A units

12 Model B units

8 Model C units

4 Model D units

4 Model E units

6 Model A units and 2 Model D units

Furnace capacity, indicated by process weight rates of the models, range from 0.5 to 0.65-ton per hour for the kettle type and 0.5 to 1.0-ton per hour for the reverberatory type. Kettle furnaces having capacities as high as 1.0-ton per hour are also in use as shown in Table VI-3.

PROPOSED USE OF MODELS

The models developed here are believed to approximate representative industrial, secondary zinc, sweating processes that emit deliquescent, corrosive chlorides. The approximations are believed close enough to bring out the general make-up and physical characteristics of those emissions. Therefore, the models should be suitable for preliminary studies of emission control concepts. For advance work involving prototype and demonstration devices, data directly applicable to specific existing plants should be obtained.

Table VII - 1 (page 1 of 2) - Zinc Sweat Process Model Units

		1	2	3	4	5	6	7	8	9		10		11	12
Model Unit Ident. Letter	Furnace Type	Emitting Process-Equipment Unit	Type of Scrap Material Processed	Type of Flux Applied	Process Weight Rate		Emission Point	Emission Factor	Particulate Emission Rate	Particulate Composition - %					
					ton scrap/hr per furnace	lb flux/hr per furnace		lb. particulate per ton Process Mat'l.	lb/hr per furnace (Col. 4 X Col. 7)	$ZnCl_2$	ZnO	H_2O in $ZnCl_2 \cdot 4H_2O$	H_2O of Deliquescence	Other Metal Chlorides and Oxides	Carbonaceous Particulates
A	Kettle Furnace	Melting kettle	Residual scrap, mixed (no organic material)	Residual $ZnCl_2$	1/4	10	Top of melting kettle	24.5	6.1	34	40	18	4	4	0
B	Kettle Furnace	Melting kettle	Residual and metallic scrap, including organic mat'l., mixed	Residual $ZnCl_2$	1/4	8	Top of melting kettle	24.5	6.1	28	40	15	3	4	10
C	Kettle Furnace	Melting kettle	Metallic scrap, mixed -containing organic mat'l.	$ZnCl_2$	0.65	0.66	Top of melting kettle	10.8	7.0	5	77	3	1	4	10
D	Reverberatory Furnace	Sweating chamber	Residual and metallic scrap, incl. organic mat'l., mixed	Residual $ZnCl_2$	1/2	16	Flue and hooded furnace openings, combined.	.32	16	15	65	8	6	6	0
E	Reverberatory Furnace	Sweating chamber	Metallic scrap, mixed -containing organic mat'l.	$ZnCl_2$	1	1	Flue and hooded furnace openings, combined.	13	13	4	89	2	1	4	0

Table VII-1 (page 2 of 2) - Zinc Sweat Process Model Units

Model Unit	1 2 Particle Size and Particle Size Distribution		3 4	5 Exhaust-Effluent	6 Effluent Flow Factor	7 Effluent Flow Rate	8 Process Bath Temp.	9 Exhaust Effluent Temp.
Ident. Letter	$ZnCl_2$ and ZnO formed from vapor	$ZnCl_2$ and ZnO entrained from skimmings	Carbonaceous Particulates	Gas Composition	Cu.ft.Effl. per ton Process Material	SCFM (Col.4,p.1 X Col.6, p.2 ÷ 60)	°F	°F
A	1 micron - may include agglomerates up to 10 microns. Makes up 60% of particulate emissions.	Larger than 10 microns. Makes up 40% of particulates.	None	78% N_2 21% O_2 (dry air)	200,000	830	900	150
B	Same except particles in this size range make up 55% of particulates.	Same except particles in this size range make up 35% of particulates.	Particles range from micron-size droplets to visible fly ash. (10% of particulate emissions.)	78% N_2 21% O_2 .1% CO_2 .1% CO .1% H_2O	Same	Same	Same	150
C	Same as B.	Same as B.	Same as B.	Same as B.	Same	2,200	900	150
D	Same as A.	Same as A.	None	73-78% N_2 3-21% O_2 0- 8% CO_2 0-15% H_2O	800,000	6,700	1000	190
E	Same as A.	Same as A.	None	73-78% N_2 3-21% O_2 0-8% CO_2 0-15% H_2O	400,000	6,700	1000	190

Chapter VIII

Emission Control Systems - Past, Present and Conceptual

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Chapter VIII

Emission Control Systems - Past, Present, and Conceptual

EXHAUST SYSTEMS

Exhaust effluents from kettle sweat-process furnaces are collected by means of hoods that cover and enclose melting kettles. Openings in these hoods are provided to allow process operations such as charging, fluxing, and skimming. When they are not in use these openings are covered to minimize air infiltration. Usually a plant incorporates several such furnaces that are operated at the same time. Typically, ducts connected to the tops of furnace hoods carry effluent to a header through which the combined effluents are carried to emission control (gas cleaning) equipment. Dampers in the duct system allow furnaces not being used to be closed off and also allow effluent to be carried directly to the stack when clean scrap is being processed or during an emergency shutdown of the gas cleaning equipment. Drafts are induced by exhaust fans of the emission control equipment and/or by the natural draft characteristics of the stack.

Effluents from the reverberatory sweat-process furnace are collected by means of the furnace flue and hoods covering other openings in the furnace. These effluents, which may be combined with those of other reverberatory or kettle furnaces, are carried to gas cleaning equipment or a stack through duct systems similar to that described above.

Effluents from rotary sweat-process furnaces are exhausted through the furnace flues of each furnace directly to an afterburner, thence to a stack.

PAST ATTEMPTS TO CONTROL SWEAT-PROCESS EMISSIONS

Gas-cleaning devices used in past attempts to control emissions from zinc-sweat processes are described below, with reasons for discontinuing their use. Except as otherwise noted, all of this equipment had been applied to processes approximating combinations of Models A and B (Chapter VII), residual scrap being contained in furnace charges, resulting in particulate emissions of high chloride content.

SCRUBBER, JET IMPACT (PLAIN WATER)

This (pilot model) scrubber had a rated capacity of 500 CFM. It operated with a pressure drop of 27.5 in. w.g. at gas flow rates around 430 SCFM. Collection efficiencies were satisfactory, exceeding 98 percent. Consideration of the following attributes of the equipment, however, led to discontinuance of its use:

A. Unit could not withstand corrosiveness of fumes. (Fabricating material of the unit is unknown but is presumed to be mild steel.)

B. High electric power requirement.

C. High maintenance requirement.

D. High water consumption.

E. Problem of polluted waste water disposal.

F. No performance guarantee.

SCRUBBER, VENTURI (PLAIN WATER)

This scrubber had a rated capacity of 2200 CFM. It operated at pressure drops between 46 and 58 in. w.g. at gas flow rates of approximately 2000 SCFM, obtained by means of a fan with a 50-HP motor. Collection efficiencies between 92 and 99% were attained. This system was discontinued because cost of the electric power was considered prohibitive for the limited gas-handling capacity.

SCRUBBER, PACKED TOWER (PLAIN WATER)

The maximum collection efficiency of this equipment was between 60 and 65%; at this efficiency the local code could not be met.

BAGHOUSES

Bag filters made of modacrylic, acrylic, cotton, and silk were applied in efforts to control emissions. Use of all of these was discontinued because fabrid endurance was limited to a maxiumum of 1 month. The bags failed as fabrics corroded (became pasty and disintegrated). Although process and emission data were not obtained for these emission control attempts, it is believed that the processes approximated Models A and B, kettle furnaces being used with resulting emissions of high chloride and low carbonaceous content.

Orlon (acrylic) fabric bag filters have been used to collect particulate emissions from sweat processing of metallic scrap materials in reverberatory furnaces as shown in Table 87 of APEM. Data were not provided on flux applied, organic material in the charge, and any resulting chloride and carbonaceous content in the emissions. The considerable amount of particulate emissions (shown by data in Table 87) indicated that substantial quantities of impurities were being removed from metal being sweated and that flux would have been applied to help effect that removal. Also, organic material was probably contained in the charge because some coating or content of organic material is characteristic of scrap items other than clean castings. Since bags were not blinded by the deliquescent effects of chloride or by carbonaceous particulate it seems likely that chloride content was low and that incineration of organic material was nearly complete. It thus appears that process and emission conditions of this baghouse application approximated Model E.

Endurance of the Orlon bags in the above application was not reported. However, the test results indicate that a baghouse system can be used satisfactorily to collect emissions from zinc-sweat processing in reverberatory furnaces where particulate chloride concentration is low enough and effluent temperature is high enough to prevent harmful deliquescent effects.

Orlon bag filters have been used for collecting emissions from secondary brass processes, where particulates were mostly ZnO. Apparently the bags were satisfactory for this usage. (AE, Nov. '67)

During this study, no direct information was obtained on modacrylic or acrylic bag filters in current usage with secondary zinc or brass processes. It appears that polyester fabric is preferred in current practice.

Glass cloth bag filters have been used to control emissions from reverberatory sweat processing of zinc scrap, as reported in APEM, p. 299. Their use was discontinued because glass fibers failed to withstand abrasion of threads during bag cleaning.

Bag filters cannot be used where carbonaceous emissions are at a level that would pose a fire hazard and where droplets of liquid carbon compounds would blind the bags.

EMISSION CONTROL SYSTEMS IN CURRENT USE

SCRUBBER, IMPINGEMENT PLATE (PLAIN WATER)

A scrubber of this type is being used to clean exhaust effluents from a plant system that consists of several units approximating Model C. Materials processed consist of metallic scrap mixtures including unplated and plated castings and fabricating scrap. Content of organic materials and other impurities is moderate orcrelatively low. Amounts of applied $ZnCl_2$ flux and resulting chloride emissions are of an intermediate or relatively low level, as Model C indicates.

This three-stage scrubber is similar to that described in Control Techniques, para. 4141214. Nozzles, plates and baffles are stainless steel. The scrubber housing is coated internally with polyvinylchloride. Pipes that circulate scrubbing fluid are of mild steel. Gas is exhausted from the scrubber by a fan requiring a 45-1/2 HP motor. A 2-HP motor is used for pumping scrubbing water.

The scrubber is operated at all times that metal is being melted, fluxed, and worked. Therefore, carbonaceous emissions that occur during initial heating of charged material are collected, as well as $ZnCl_2$ and ZnO emissions occuring during subsequent fluxing and working of the bath.

The scrubber operates with a pressure drop of 11 in. w.g. at a gas flow rate of 16,000 CFM.

Collection efficiency of this equipment has not been determined by particulate sampling tests. Observations of the plume, indicate that 90 to 95% of particulate is collected 90% of the time. Observations of the plume under process conditions known to be conducive to emission of $ZnCl_2$ and ZnO, individually, indicate that the scrubber collects $ZnCl_2$ very efficiently but that it is not very efficient in collecting ZnO. The 10% of the time when collection efficiency is apparently less than 90% is probably accountdd for by excessive ZnO emissions occuring at high molten metal bath temperature.

The stainless steel and PVC-coated parts of the scrubber have satisfactorily withstood corrosion by the scrubbing fluid, although infrequent failures of the nozzles apparently have been caused by stresses involving welds; and there has been minor corrosion of the mild steel pipes. These results tend to confirm that emissions from the processes involved are of low chloride content (probably around 5%, as assumed for Model C, or less).

The low resistance of stainless steels and of iron to corrosion by $ZnCl_2$ solutions (Perry 4th ed., pp. 23-29, 30) indicates that those materials would not withstand that corrosion except at low $ZnCl_2$ concentrations. Because of low corrosion resistance, therefore, the scrubber could be used satisfactorily to control emissions only from the processing of relatively clean scrap, that does not entail considerable flux application.

Use of this scrubber is further restricted by emission of ZnO in excess of the capacity of the scrubber for satisfactory removal, which occurs at high molten metal temperatures. Thus, emissions from processing residual scrap cannot be satisfactorily controlled because high temperatures are required to sweat-process that type of scrap. Also, in sweating some metallic scrap, particularly with considerable unmeltable attachments, temperature distribution within the bath is uneven, with high temperature regions emitting ZnO excessively. Using instruments to obtain meaningful bath temperatures under this condition is generally precluded, so that maintaining satisfactory temperatures and mixing the bath depends on visual and manual techniques of the operator. This dependency further restricts the range of metallic scrap that can be processed since manual techniques are of limited accuracy in maintaining bath temperatures at levels where ZnO emissions are controllable.

Passage of emitted carbonaceous particles through the scrubber has been evidenced by deposits of small quantities of tar-like substances (probably mixtures of hydrocarbons and ZnO) on the scrubber exhaust fan and fan closure. These deposits resulted in imbalance of a previously used fan, which caused destructive vibration. This problem was overcome by replacing that fan with a "standard duty wheel".

The tar-like deposits have not occured during several months since this replacement. These carbonaceous particulate emissions, controlled at low levels by selection of relatively clean scrap, probably do not pose an air pollution problem. However, the limited capacity of the scrubber to control carbonaceous particulate emissions, shown by the tar-like deposits, restricts the content of organic material that can be tolerated in scrap material processed.

In summary, this scrubber is limited to handling emissions from the processing of selected types of scrap materials, excluding (1) metallic scrap that contains more than small amounts of organic impurities, (2) all residual scrap, (3) metallic scrap having large amounts of unmeltable attachments. These limitations were determined through experience with kettle-furnace processing. Although no information was obtained on use of the scrubber with reverberatory furnaces, this scrubber would be relatively ineffective in controlling the high rates of ZnO emission that are expected from processing most scrap materials in reverberatory furnaces. A further limitation is that there is no known use for the scrubber waste slurry.

SCRUBBER, VENTURI (PLAIN WATER)

This study indicates that venturi scrubbers are not being used in the secondary zinc industry. However, effluents containing particles that consist mostly of ZnO, emitted from a secondary brass plant, are being controlled by a venturi scrubber (MC, 6/70). These emissions are from reverberatory furnaces wherein "blowing" operations are conducted. (See pages VI-12, 13).

Part of this venturi system is made of stainless and part of mild steel. The system can operate with a total pressure drop up to 54 in. w.g. at gas flow rates up to 23,000 ACFM.

Operation of the system has been satisfactory. Emission tests have shown collection efficiencies between 92 and 99% at effluent gas temperatures around 500°F and at a resulting saturated gas temperature of 90°F. There has been no corrosion or abrasion of either the stainless or mild steel parts of the system. The ZnO apparently provides a protective coating effect over the bare metal of the scrubber system. (The emissions are probably of close to neutral pH.)

The system incorporates a filtering device that discharges collected particulates as wet filter cake.

BAGHOUSES

Dacron (polyester) multifilament bag filters are being used to collect emissions from a combination of several reverberatory and distillation retort furnaces. (Emission points are as indicated in Tables IV-1 and IV-2). Materials processed include contaminated die-cast scrap and galvanizers' drosses, which may contain very small amounts of chloride flux. No additional flux is applied. The collected particulate material contains about 95% ZnO and may include small percentages of chlorine as chlorides.

The installation (duct size, length, etc.) and process operations of this system are such that the effluent temperature at the point of baghouse collection is around 250°F. By maintaining this temperature and the low percentages of chlorides in particulates being collected, blinding of the bags and caking of collected material due to deliquescence are prevented. Carbonaceous emissions are prevented by virtually complete incineration of organic material in the reverberatory furnaces. The bags are satisfactorily cleaned by means of a pneumetic air shaker.

The company using this system reports that at temperatures as high as 212°F, $ZnCl_2$ particles become visibly wet and might blind bags by adsorption of atmospheric moisture. Hence, the higher effluent temperature of 250°F is maintained.

This baghouse installation incorporates about 1700 square feet of cloth surface, with an air-to-cloth ratio of 2 to 1, maximum. Flow through the system is about 28000 cfm, and pressure drop across the bags is 2 in. w.g. A 50-HP motor drives the exhaust fan. The system collects about 350 pounds of particulate per day.

In another installation, a baghouse using polyester fabric bags collects emissions from reverberatory furnaces where contaminated die cast scrap is processed without applying flux. Molten metal from this furnace is subsequently distilled. Again, organic material in charged scrap is satisfactorily incinerated in the reverberatory furnace, and baghouse collection is satisfactory.

Experience in baghouse applications indicates that polyester fabric is the most acceptable bag material in present use for collecting emissions from zinc-distillation processes and limited zinc-sweat processes.

Limitations of polyester-fabric filters have not been established, but it seems evident that at maximum atmospheric moisture content usage would be limited to certain ranges of chloride concentration in the emitted particulate, those ranges being defined with effluent temperature and air-to-cloth ratios as the principal parameters. The experience reported above indicated that a maximum $ZnCl_2$ concentration between 2 and 5% at an effluent temperature of 250°F and a maximum air-to-cloth ratio of 2 to 1 falls within an acceptable range.

Model E probably represents marginal process and emission conditions, in which a baghouse might or might not perform satisfactorily.

Polyester-fabric bag filters could not be used where charges containing considerable amounts of residual scrap are being sweat processed in either reverberatory or kettle furnaces because of chlorides that would be emitted. Use of the bag filters would be further precluded where metallic scrap charges containing significant organic material are processed in kettle furnaces because of carbonaceous, as well as chloride, particulate likely to be emitted. Thus all models in Table VII-1 except Model E seem precluded from emission control by means of baghouses.

ELECTROSTATIC PRECIPITATORS

An electrostatic precipitator is used to clean exhaust effluents from processes consisting of combinations of units approximating Model A, B, and D. Charges to furnaces consist mainly of residual scrap mixtures having considerable residual flux content. Small amounts of metallic scrap containing organic materials may also be included. Therefore, chloride content of emitted particulate is high, and small percentages of carbonaceous particluate may also be emitted.

This precipitator has the general configuration of the flat-surface type shown in Control Techniques Figure 4-45. Electric conductors in the precipitator that are exposed to emissions are made of stainless steel. An electric heater prevents accumulation of moisture in the precipitator.

Electric power consumption by the precipitator is low, most being consumed by 15-HP fan motor used to exhaust the precipitator, very little being consumed at the electrodes.

During operation, the pressure drop is 0.3 in w.g. across the total exhaust and emission control system at an effluent flow rate of 15,000 ACFM and 120°F effluent temperature.

Results of an emission test showed a collection efficiency exceeding 98%, reducing emissions to less than .01 Gr./SCF, with about 57 pounds of particulate per hour being collected at a total process weight rate of about 2.4 tons per hour.

Some corrosion of the stainless steel electric conductors has resulted from contact with the collected chloride particulates. The extent of this corrosion is significant, but not so great as to prevent use of the system.

There is some possibility that carbonaceous particles, if present in emissions being collected, might be ignited by electrical discharges within the precipitator.

The presence of $ZnCl_2$ probably imparts electrical conductivity to the particulates that enables their efficient collection in electrostatic precipitators. Because of high resistivity, there is probably a limit on concentration of ZnO in particulate at which precipitator collection efficiencies are satisfactory. (Donoso p. 8).

Following are the principal limitations and disadvantages of the electrostatic precipitator for the application described:

A. Corrosion of stainless steel parts.

B. Possible ignition hazards where charges contain organic material and where furnace conditions are not conducive to complete incineration of those materials. (See Chapter VII)

C. Lack of a known use for the mixtures of $ZnCl_2$ and ZnO with small amounts of other substances collected in the precipitator.

D. Restriction of efficient collection to a certain range of particulate composition and effluent temperature. High ZnO concentration and high temperature could reduce electrical conductivity and cause inefficient collection; high $ZnCl_2$ concentration (with low ZnO content) could cause excessive corrosion.

AFTERBURNERS

Exhaust effluents from rotary furnaces are passed through afterburners to burn carbonaceous particulate and gaseous emissions. Additional gas cleaning is usually not done because concentration of noncarbonaceous emissions in these effluents is low.

One problem was reported on afterburner usage. At times during sweat processing with afterburners in operation, significant carbonaceous emissions do not occur. Because no control devices or methods are available to detect this condition and responsively stop afterburner operation, fuel is wasted during such periods.

CONCEPTUAL EMISSION CONTROL SYSTEMS

Information is given here concerning the only system investigated during this study that has been tested as a new approach to controlling emissions from zinc-sweat processes. In the following chapters on Conclusions and Recommendations, emission control concepts will be developed further, based on the total findings presented in this report.

The conceptual system that had been tested was a laboratory-scale modification of the system for removing solid and mist particles shown in DEP 3/67. In this modified system, part of the effluent from a zinc-sweat process approximating

Model C was filtered through a water-irrigated, polyester-felt diaphragm (approximately 12-inches diameter and 1/2-inch thick). During the tests, process conditions were varied to yield emissions having the composition characteristics shown below:

Applied Process Conditions	Resulting Characteristics of Particulate Emission Composition
A. High $ZnCl_2$ flux content in charge and normal molten metal bath temperature.	High Chloride ($ZnCl_2$) content.
B. High molten metal bath temperature and no $ZnCl_2$ flux in charge.	High ZnO content.
C. High organic material (oil) content in charge.	High carbonaceous (oil droplet) content.

Findings of this test were limited to these visual observations:

A. The irrigated filter was very effective in removing $ZnCl_2$ particulate emissions generated by process condition A, as shown by clean air downstream of the filter.

B. The irrigated filter was only partly effective in removing ZnO particulate emissions generated by process condition B, as shown by visible smoke downstream of the filter and white clouding of the scrubbing water, both occurring at the same time.

C. The irrigated filter was blinded very quickly, increasing greatly the pressure drop across the filter, by oil droplets emitted during process condition C. After the test, notable white ZnO could be seen on the downstream side of the filter, while greater intensity of the black burned-oil color appeared on the upstream side.

Although no quantitative data were available from this test, the data in the reference article are significant. In a pilot unit, thin, water-irrigated, felt filter pads were tested. The effluents being cleaned were exhaust gases from pigment calciners that contained sulfuric acid mist and TiO_2 pigmentary particles at about 167°F temperature. Filter pads made of polyester, polypropylene, and polyacrylonitrile fibers were tried. The housing in which the filter was mounted and thorough which the effluent passed was made of polyester glass resin.

In several tests in which polyester and polypropylene felt filters were used (individually), collection efficiencies were reported between 94 and 100% for TiO_2 removal; and between 83 and 94% for acid mist removal. During these tests, effluent gas flow rates ranged from 75 to 170 ft/min.[(cu ft/min)/sq ft] and pressure drops were from 6.5 to 9.6 in. w.g. The reference article comments that a minimum flow rate of 8 gallons of spray liquor per 1,000 cubic feet of gas was required for high mist removal. Loading of acid mist in gas being cleaned was as high as 1.74 grains/per standard cubic foot.

The relative suitability of the felt materials tried for this application was not discussed in the reference article; endurance of a polyester material was especially noted, however. This material lasted until its support screen failed after a 59-day test period. It was also noted that polypropylene and polyester are very much more resistant to wetting than polyacrylonitrile, with polypropylene slightly more resistant than polyester. (As noted above, high collection efficiencies were attained with both polypropylene and polyester felt filters.) A PVC-coated glass mesh screen provided satisfactory support for the filter pad.

The test results shown above, considered together, indicate that $ZnCl_2$ particulates can be removed from zinc sweat process effluents at very high efficiencies and low energy consumption (low pressure drop) by means of this conceptual system.

The principal limitations of the irrigated fibrous felt system for cleaning zinc sweat process effluents are blinding of the filters by carbonaceous particulates in effluents being cleaned, and low efficiency of ZnO particulate removal.

Chapter IX

Conclusions

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Chapter IX

Conclusions

PROCESSES OF SECONDARY ZINC PRODUCTION

EFFECTS OF PROCESSES ON EMISSIONS

The effects of processes, as defined by the type of furnace used, on resulting emissions are characterized and compared as follows:

Emission Characteristics of Reverberatory Furnaces

1. Carbonaceous emissions are controlled satisfactorily by incineration of organic material within the furnace, where furnace design and operation are satisfactory.
2. Noncarbonaceous particulate emission rates are higher than those of kettle or rotary furnaces processing comparable charges.
3. Effluent flow rates are higher than those of kettle furnaces processing comparable charges.

Emission Characteristics of Rotary Furnaces

1. Carbonaceous emissions are not controlled satisfactorily by incineration within rotary furnaces of current design but are controlled satisfactorily by application of afterburners.
2. Noncarbonaceous emissions are not significant, where flux is not applied and where furnace design and operation are satisfactory.
3. No data were obtained on effluent flow rates of rotary furnaces.

Emission Characteristics of Kettle Furnaces

1. Carbonaceous emissions are not controlled satisfactorily by incineration within the furnace but are usually held at levels low enough that afterburning is not required by charging scrap material mixtures that do not contain large amounts of organic materials.

2. Emissions of noncarbonaceous particulate are significant when the furnace charge contains significant amounts of flux and inorganic impurities, but are lower than those of reverberatory furnaces processing comparable charges.

3. Effluent flow rates are lower than those of reverberatory furnaces processing comparable charges.

Emission Characteristics of Distillation Furnaces

1. Carbonaceous emissions do not occur.

2. Emissions of noncarbonaceous particulate are significant but are limited to nearly pure ZnO (no significant chloride content).

3. No data were obtained on effluent flow rates from distillation furnaces.

SELECTION OF PROCESSES TO MINIMIZE EMISSIONS

Emission characteristics of the several types of secondary zinc processing furnaces can be applied by selecting specific combinations of furnaces to minimize emissions and effluent flow. This approach to emission control is effective in certain applications, as shown by two notable examples:

1. Scrap containing considerable organic material is processed without flux in reverberatory furnaces, and the resulting sweated crude zinc alloy is distilled to obtain pure zinc. In this way, carbonaceous and chloride emissions are prevented and noncarbonaceous emissions (free of chlorides) that occur can be collected in conventional baghouses.

2. Scrap containing considerable organic material is processed without flux in rotary furnaces with afterburners. The resulting crude zinc alloy is then processed further with application of relatively small amounts of flux in kettle furnaces. In this way, carbonaceous emissions are controlled and noncarbonaceous emissions are minimized, and thus the requirement for gas-handling capacity of any equipment used to clean those effluents is reduced.

Minimizing emissions through furnace selection is well established and appears to have been optimized in the secondary zinc industry. Emissions cannot be controlled completely by this approach, however, as the examples illustrate. A further example of the limits of this approach to emission control is that high-chloride-content particulates are emitted from processes of sweating residual scrap where considerable flux is present, regardless of furnace selection. (Pretreatments to remove chlorides from residual scrap are of limited economic practicality.) Besides considerations of emission control, process selection depends on materials to be processed, products to be made, and process economics. Conservation of alloy metals (mainly aluminum and copper) may be a further consideration in process selection. These metals are utilized automatically where zinc alloy is sweated from scrap, then realloyed to meet a zinc alloy specification. The alloy metals might be partly or wholly lost where scrap-derived crude zinc alloy is distilled.

It is concluded that, with optimum process selection to minimize emissions, problems remain in control of emissions from processes represented by the process models developed in Chapter VII.

EMISSIONS FROM SECONDARY ZINC SWEAT PROCESSES

EMISSION CHARACTERIZATION

Emissions from zinc sweat processes may be classified in two general catagories:

1. Emitted mixtures mostly of carbonaceous particulate and gaseous substances. (Noncarbonaceous particulates might be present, but only in minor amounts.) These mixtures occur most characteristically in emissions from rotary furnaces.

2. Emitted mixtures mostly of noncarbonaceous particulate substances, principally $ZnCl_2$ and ZnO. (Carbonaceous particulate and gaseous substances might be present in amounts which, though relatively small, could be significant in emission control.) These mixtures occur most characteristically in emissions from kettle and reverberatory furnaces.

Conclusions in the paragraphs that follow pertain only to the preponderantly noncarbonaceous emissions of the second catagory.

Values approximating data that characterize these sweat-process emissions were developed in Chapter VII and are shown for process model units in Table VII-1.

Following are the approximate ranges of quantitative properties characterizing these emissions:

1. Emission factors range from negligible for processing clean scrap in kettle furnaces to around 30 pounds of particulates emitted per ton of process material for processing residual scrap in reverberatory furnaces.

2. In typical sweat processing of zinc scrap materials, the percentages of equivalent anhydrous $ZnCl_2$ in particulate emissions range from none to around 34%, the percentages of ZnO from around 40% to 90% or more, and the percentages of carbonaceous particles from none to around 10%.

3. Emitted particles of $ZnCl_2$ and ZnO are mostly around 1-micron diameter or less; these small particles result from vaporization of $ZnCl_2$ flux and metallic zinc followed by (1) condensation of $ZnCl_2$ vapor to liquid droplets that solidify as cooling takes place and (2) atmospheric oxidation of zinc vapor to solid ZnO particles. Some of the emitted particles of these compounds may be somewhat larger than 1 micron because of agglomeration. Also, larger particles of these and other oxides and chlorides are emitted through entrainment of pulverulent material in the residue-flux mixture that forms atop the process bath.

CORRELATION OF CHARGED MATERIALS WITH EMISSION COMPOSITION

Since chloride emissions result from chloride flux in charges to zinc sweat processes, and ZnO emissions result in large part from metallic zinc charged to those processes, the following relationships would hold:

A. The particulate ratio $ZnCl_2/ZnO$ increases as the charge ratio $ZnCl_2/Zn$ increases.

B. The particulate ratio Cl^-/Zn^{++} increases as the charge ratio $ZnCl_2/Zn$ increases.

where

$$\underline{\text{Particulate ratio } ZnCl_2/ZnO} = \frac{\text{amount of } ZnCl_2 \text{ in emitted particulates}}{\text{amount of ZnO in emitted particulates}}$$

$$\underline{\text{Particulate ratio } Cl^-/Zn^{++}} = \frac{\text{amount of } Cl^- \text{ in emitted particulates}}{\text{amount of } Zn^{++} \text{ in emitted particulates}}$$

$$\underline{\text{Charge ratio } ZnCl_2/Zn} = \frac{\text{amount of } ZnCl_2 \text{ in charge}}{\text{amount of metallic Zn in charge}}$$

These relationships would apply where other process conditions are constant. Although these relationships were indicated by results of this study, data were not sufficient for developing them as equations or graphical presentations.

EVALUATION OF EMISSION DETERMINATIONS AND PROCESS MODELS

The conclusions characterizing emissions and relating them to process models were derived from a small **sampling** of data; where data were not available, theoretical considerations were applied. Deficiencies in data could be enumerated from information on formulating process models in Chapter VII. Two such deficiencies are noted here:

1. No chemical analyses were obtained on emissions from metallic scrap processing. All available chemical analyses applied to emissions from residual scrap processing.

2. All data on amounts of applied flux were approximations; flux applied to processes was not weighed, and residual scrap was not chemically analyzed to determine flux content before charging to sweat furnaces. The approximations were based on familiarity of plant operators with usual processing techniques and on published analyses of residual scrap.

The following conclusions pertain to the process models that were derived from the process and emission determinations of this study and shown in Chapter VII:

1. The process models indicate the general makeup of emissions from representative zinc-sweat processes. Values shown for the models approximate characteristics of those emissions closely enough that they may be used in initial screening and evaluating studies of emission control concepts leading to development and testing of pilot equipment.

2. The models establish a format for any further data gathering needed for research and development.

3. Because of the limited data sampling, **it would be** beneficial to obtain additional data to confirm and enhance the accuracy of the models.

4. Complete data on emissions and related processes would be needed for design of prototype or demonstration equipment. These data should be obtained at the plants where this equipment would be tested.

EMISSION CONTROL SYSTEMS

CONTROL OF HIGH-CARBON-CONTENT EMISSIONS BY CURRENT TECHNOLOGY

The preponderantly carbonaceous emissions, characteristic of rotary-furnace sweat processing of contaminated zinc die-cast scrap, are controlled with afterburners. Only one limitation of this emission control system was indicated during this study. That is, fuel combustion efficiency of the afterburners is limited by lack of devices and/or methods for stopping their operation when carbonaceous emission rates reach insignificant levels.

CONTROL OF LOW-CARBON-CONTENT EMISSIONS BY CURRENT TECHNOLOGY

Equipment used in past and present attempts to control emissions of relatively low carbon content (represented by Models A through E of Chapter VII) is of limited effectiveness. Principal limitations are shown as follows:

Corrosion of Metals by High-Chloride-Content Emissions

Emissions having high chloride concentration as represented by Models A, B, and D, cause considerable corrosion to mild steel and stainless steel parts of emission control equipment. This limitation has been experienced with plain-water scrubbers and electrostatic precipitators. Where chloride concentration of emissions is low enough these corrosive effects are tolorable.

Blinding of Fabric Filters by High-Chloride-Content Emissions

Emissions having high chloride concentration, as represented Models A,B, and D, cause blinding of fabric filters due to deliquescence of $ZnCl_2$. This limitation has been experienced with bag filters. Another effect of deliquescence of $ZnCl_2$ is corrosion of some organic-fiber, bag filter materials by collected particulates. Bag filter blinding (and conversely the range of conditions in which bag filters are useful for collecting emissions) is mainly a function of $ZnCl_2$ concentration in particulate emissions and effluent temperature. Use of higher effluent temperatures reduces deliquescence, but this practice is limited by temperature resistance of the bag material. (Carbonaceous particulates, as emitted from Model B, might also contribute to bag blinding.)

Wear of Fibrous-Glass Bag Filters

The usual fibrous-glass fabric bag filters, when used to collect low-chloride-content emissions (represented by zinc-distillation processes and by model E), do not withstand abrasive wear of woven threads that occurs during bag cleaning.

Carbonaceous Deposits in Emission Control Equipment

Carbonaceous emissions, as represented by Models B and C, may cause oily or tarlike deposits in gas cleaning equipment. This problem has been experienced at exhaust fans of plain-water scrubbers, but has been reduced to a manageble level by fan selection. Carbonaceous deposits could also occur in baghouses and electrostatic precipitators.

Ignition Hazard

Carbonaceous emissions, as represented by Models B and C, could be ignited in emission control equipment, where carbonaceous deposits accumulate and at intermittent periods when carbonaceous emissions occur at higher rates than indicated for the models . Bag filters and electrostatic precipitators appear susceptible to this hazard.

Resistivity of Particulates Outside the Collecting Range of Electrostatic Precipitators

The range of particulate emission compositions and the corresponding range of process conditions wherein particulates can be collected at satisfactory efficiencies in electrostatic precipitators are not known. Effectiveness of electrostatic precipitators depends largely on resistivity of particles being collected, a property that varies with composition of particulate emissions. Therefore for some particulate compositions collection in precipitators probably would not be satisfactory.

Blinding of Irrigated Felt Fabric Filters by Carbonaceous Particulates

Carbonaceous emissions, represented by Models B and C, cause blinding of felt filters irrigated with plain water.

PROBLEMS OF UTILIZING AND DISPOSING OF COLLECTED PARTICULATE MATERIAL

Commercial usage of collected particulates having less than around 95% ZnO has not been determined. Where large amounts of chlorides are present in the collected particulates, disposal of this material presents problems because the chloride constituents are corrosive.

AVAILABILITY OF DATA FOR PHASE II WORK

The data obtained during this study apply most substantially to sweat processing of residual scrap and mixtures of residual and metallic scrap with chloride flux being contained in charges and with resulting emissions containing considerable chloride particulates. These data are therefore the most available for subsequent (Phase II) work.

CHAPTER X

Emission Control Concepts

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Chapter X

Emission Control Concepts

CONCEPT OF PROCESS MODIFICATION TO REDUCE NON-CARBONACEOUS EMISSIONS, BASED ON FINDINGS OF THIS STUDY

GASEOUS FLUXING AND WORKING OF SEALED PROCESS BATHS

To minimize the problems of controlling the non-carbonaceous emissions that result from fluxing and working zinc-sweat process baths after any organic material has been burned off, it would be desirable to minimize both particulate emission rates and effluent flow rates. In an ideal system for accomplishing this, the bath would be contained in a sealed chamber and heated by conduction or radiation. Such a system would minimize (1) oxidation of molten metal due to contact with moving air, (2) entrainment of particles from the flux-residue mixture that accumulates atop the process bath, and (3) volume of effluent gas (infiltrated air being excluded and no fuel combustion products being added to the effluent). In current practice. the approach to this ideal is limited mainly by the need to conduct operations on the process bath such as applying flux, stirring, and skimming.

The ideal process defined above might be approached by modifying current processes as follows: After the charge is melted and most of any organic material in the charge is burned off, the bath would be enclosed to seal out air. The only opening in the bath closure would be a vent for exhausting effluent. Gaseous chlorine would be lanced into the process bath causing formation of $ZnCl_2$, as Cl_2 reacts with molten zinc. ($AlCl_3$ gas and $MgCl_2$ solid would also be formed in smaller amounts.)

Thus $ZnCl_2$ flux would be formed deep beneath the bath surface.

In this conceptual process, chloride emissions would be reduced since the procedure would eliminate the vaporization loss that occurs immediately when $ZnCl_2$ is applied to the process bath surface, as in current processing. Air infiltration and resulting particulate entrainment would be reduced, since the closure would not be opened for application of flux and for manual mixing of flux into the bath. The bath would be agitated and mixed by gas bubbling through. To increase this effect, if needed, inert gas such as N_2 might be lanced in addition to the Cl_2. To increase this effect further, determination might be made of the positions of the lances with respect to the vessel containing the bath, and the flow rates of the lanced gases that would optimize stirring effects. Initial tests might be made of lances installed projecting into the side of a chlorinating vessel (which might have a general vertical, cylindrical shape with hemispherical bottom) so as to apply the gases in a direction between radial and tangential, at controlled flow rates.

Fluxing and working the bath by this chlorinating method might be done in the original melting furnace (modified to suitably enclose the bath after burning off any organic material in the charge) or it might be advantageous to transfer the bath from the melting furnace to a separate vessel that could be closed during chlorination. This transfer of molten metal could be made with ladles or by means of a launder or piping system using gravity or mechanical pumping.

Since the reaction of Cl_2 with the molten metals would be exothermic, it probably could be conducted in a relatively simple vessel, with no provision for applying additional heat except perhaps to the lances, where heat might be needed to prevent solidification of metal at times when gases are not being applied.

It appears possible that most, if not all, of the operations of fluxing and working process baths might be done by means of this process modification (although provision would have to be made for skimming baths), and that by this means particulate emissions and effluent flow could be reduced considerably.

This process modification appears to be potentially applicable to processing all metallic and residual scrap. Flux would generally be formed by lancing with chlorine. However, where residual flux content of a scrap charge is sufficient for fluxing needs, N_2 alone might be lanced to accomplish the needed agitation and mixing of the enclosed process bath.

CONCEPTS OF EMISSION CONTROL SYSTEMS, BASED ON FINDINGS OF THIS STUDY

High-carbon-content emissions from zinc sweat processes can be controlled satisfactorily with afterburners. Therefore, the principal objective of research and development pertaining to cleaning the exhaust effluent gases from secondary zinc processes should be to develop devices capable of cleaning effluents having low carbon content but with significant chlorides; such emissions may be defined as those from any combination of Process Model Units A through E (Chapter VII). The most urgent need for such devices is for application to emissions from processing charges that contain residual scrap with or without metallic scrap.

The above considerations lead to the following criteria for gas cleaning devices to be developed:

1. The devices should be capable of removing the following particulate constituents from effluents:

   a. Carbonaceous substances (liquid and solid) present as relatively small fractions of total particulate (around 10% average, with variations from 0 to 20%).

   b. $ZnCl_2$ (0 to 40% of total particulate).

   c. ZnO (0 to 100% of total particulate).

2. These constituents should be removed in a minimum number of stages (gas cleaning equipment units).

To meet these criteria several concepts of gas cleaning devices are presented below.

CHLORIDE CONDENSATION SYSTEMS

The occurrence of a liquid state during formation of $ZnCl_2$ particulate (see Page V-12) suggests that settling chambers, condensers, or reflux columns might be developed for removing $ZnCl_2$ from effluent gas and separating that chloride from ZnO.

In a system incorporating a settling chamber for that purpose, effluent would be allowed to cool slowly to 689°F (the melting point of $ZnCl_2$) to increase the tendency to particle growth through condensation of $ZnCl_2$ vapor on surfaces of the initially formed particles and through agglomeration of those particles. Agglomeration would be promoted by Brownian motion (at elevated temperatures) increasing the collision and fusion of the liquid particles. The application of sonic agglomeration might be considered to further promote this effect. This system might be designed to allow particles to settle while still liquid or to allow them to cool below 689°F, after attaining suitable size, and settle as solid particles. Such a system might include two chambers: the first to maintain an elevated temperature to allow particle growth and agglomeration; the second to allow cooling and settling, then removal, perhaps through a hopper.

A condenser or reflux column used for this purpose might contain baffles and/or packings to provide surfaces on which $ZnCl_2$ droplets could impinge, collect, and flow. Heated ducts might also be used in such units to maintain the needed temperature range, while also providing surfaces for droplet impingement. If a condenser were used, liquid $ZnCl_2$ would be allowed to flow out for recovery. If a reflux column were used, liquid $ZnCl_2$ would flow back to the process bath for recycling.

Waste heat from furnaces, afterburners, or other sources in secondary zinc plants might be used to maintain the needed temperature in the conceptual settling, condensing, and reflux devices described above. For example, effluent from a reverberatory furnace might be channelled through a chamber constructed on top of that furnace. Heat transferred from the top of the furnace into the chamber might maintain the elevated effluent temperature needed to bring about the desired $ZnCl_2$ particle growth. The effluent might then be channelled to an adjacent chamber for cooling and settling.

Particles of ZnO would not have the tendency of $ZnCl_2$ to grow and agglomerate by vapor condensation and liquid fusion. It is, therefore, expected that ZnO particles would pass through the settling chamber, condenser, or reflux column, and might be collected in a baghouse, electrostatic precipitator, or scrubber. The separation, of course, would not be complete. There would be some mixing of ZnO with the $ZnCl_2$ removed in the first (settling, condensing, or reflux) stage and of $ZnCl_2$ with the ZnO removed in the second gas-cleaning stage.

Most of the carbonaceous particles would probably be removed with the $ZnCl_2$ that condenses or settles out, since the solid (fly-ash) type of carbonaceous particles would generally be relatively large and liquid carbonaceous particles would tend to agglomerate forming larger particles. With the reflux column, the collected carbonaceous material would be returned to the furnace (with $ZnCl_2$), where it might be ultimately consumed in combustion.

Ceramic materials appear most promising for construction of these systems, but metals including mild steel might be tried especially for parts like hoppers, where dry particles would be handled.

CHLORIDE SOLUTION SYSTEMS

Zinc chloride is soluble in water, and $ZnCl_2$ particles are wetted readily by liquid and vaporous moisture. In contrast, ZnO is insoluble in water and resists wetting. This comparison of properties suggests that $ZnCl_2$ particulate might be efficiently removed from effluents by means of aqueous scrubbers that operate at low energy loss (low effluent gas pressure drop); and that $ZnCl_2$ might thereby be separated from ZnO particles in the effluent, the latter requiring a high energy loss for removal in aqueous scrubbers. (See Page VIII-7). A scrubbing system for this purpose might include one or more chambers and/or towers containing water sprays, water films, irrigated packings, and/or baffles alone or in combination.

For example, a spray chamber or irrigated packed tower might prove sufficient, or such units might be used in combination. (See Control Techniques 4.4.) As $ZnCl_2$ particles emitted from a zinc sweat process passed through the scrubber, they would absorb moisture, increasing their weight and tendency to agglomerate. The resulting increased inertia would increase their interception by water drops, water films, packings, and/or baffles in the scrubber. The small ZnO particles would retain their low inertia and tend to pass through the scrubber.

The potential of the conceptual chloride solution system suggested above is further indicated by results of tests of water-irrigated diaphragm filters. (See Page VIII-13.) These tests showed that $ZnCl_2$ particulate emissions can be efficiently removed from effluents, at low energy loss, by interception at water-irrigated fibers; while ZnO, in large part, passes through.

The indicated potential of this concept is also supported by results of tests in which HCl gas was efficiently collected at low energy loss by several types of packed aqueous scrubbers (KSB).

Particles of ZnO that pass through the conceptual aqueous scrubbing system, probably with some $ZnCl_2$ retained in the effluent, might be collected in a baghouse, electrostatic precipitator, high-energy venturi scrubber, or other suitable equipment. If a dry collector such as a baghouse or electrostatic precipitator were used, it might be necessary to first dry the effluent and/or raise its temperature above the dew point. A dry bed or similar device might be used to eliminate mist. Waste heat from furnaces or afterburners in the plant might be used to raise the effluent temperature above the dew point. For example, the effluent (after passing through the scrubber) might be passed through a chamber or other heat exchange device positioned above a reverberatory furnace, thus applying heat from the furnace to the effluent. A heat exchanger might also be devised that would utilize heat from the exhaust gas of a rotary furnace afterburner for that purpose.

In devising a scrubbing system to collect $ZnCl_2$, the various wet collectors and ancillary equipment shown and discussed in Control Techniques, 4.4, should be considered. Plain water, NH_4OH, and non-foaming detergent solutions might be considered as scrubbing media for $ZnCl_2$ removal.

Scrubbing with plain water would seem to generally preclude use of irrigated filters approximating the felt diaphragm type described on Pages VIII-12,13 because of blinding by carbonaceous particles. However, other low-energy-loss scrubbers shown in the above-mentioned reference might be considered.

Scrubbing solutions of NH_4OH, maintained neutral or slightly alkaline, would probably overcome the acidic corrosion caused by hydrolysis of $ZnCl_2$ and NH_4Cl. Collection of carbonaceous particles might be increased because of reduced surface tension resulting from NH_4OH in the scrubbing solution. However, alkalinity might cause precipitation of enough $Zn(OH)_2$ to clog some types of scrubbers. Therefore, scrubbing with NH_4OH solution might restrict selection of scrubbing devices to those that resist clogging, such as spray types.

Scrubbing solutions of non-foaming detergents including NaOH and sodium phosphates might be tried in an irrigated-filter scrubber, such as the felt diaphragm type described on Pages VIII-12,13, the detergents being used to remove carbonaceous particles (mainly oil droplets) and prevent blinding of the filter. The pH of such solutions would have to be controlled to prevent $Zn(OH)_2$ precipitation. Attempts might be made to accomplish this by determining a satisfactory buffered-solution composition.

Zinc chloride and NH_4Cl collected in plain water or NH_4OH scrubbing solution, as suggested above, might be recovered. Settling and filtration might be tried to remove insoluble (mainly carbonaceous) substances. Removal of insoluble substances in this way would be mainly applicable to plain-water scrubbing systems. Resulting solutions might be evaporated, perhaps using plant waste heat, to recover the chlorides.

The efficiency of the first (scrubbing) stage of this conceptual system in removing carbonaceous emissions as well as chlorides (mainly $ZnCl_2$), would be important to determining feasibility of this system because of the possible blinding of filtering devices and the ignition hazard that would be posed by carbonaceous substances in the subsequent ZnO removal stage.

As mentioned earlier, the corrosiveness of the chlorides handled by the scrubber might be overcome by scrubbing with NH_4OH solution. Pertaining to plain-water scrubbing (as suggested above) materials that have been found satisfactory in scrubbers handling corrosive chlorides include mild steel coated with certain rubbers and plastics, fiberglass-reinforced polyester plastics, and acid-resistant brick (CEP 3/67, Donoso, KSB). Stainless steel has been used successfully for handling solutions of low $ZnCl_2$ concentration, but has corroded significantly in direct contact with collected particulate having high chloride concentration and with solutions of high $ZnCl_2$ concentration (see Pages VIII-5,6,11). Both ceramic and plastic packings have been used in scrubbers collecting corrosive chlorides. Mild steel duct work has been satisfactory for carrying emissions from furnaces to stacks and gas cleaning equipment, showing that solid $ZnCl_2$ particles do not present a corrosion problem in the absence of moisture.

Consideration might be given to including an afterburner as the first stage of this conceptual emission control system, to be operated when carbonaceous emissions are high and by-passed when not needed. Waste heat from this afterburner might be used for any of the purposes mentioned herein. Conceivably, such an afterburner might be operated as a source of heat for those purposes, even when not needed to control carbonaceous emissions.

In evaluating this concept, the effects of several variables on collection efficiency of scrubbers used to remove $ZnCl_2$ should be determined. These determinations could lead to optimizing those variables for maximum collection efficiency. These variables seem particularly pertinent:

1. Temperature of effluent entering the scrubber.
2. Concentration of $ZnCl_2$ in effluent entering the scrubber (which would tend to increase as air infiltration rate decreases). Might be expressed as grains $ZnCl_2$ per standard cubic foot.
3. Phase or phases of $ZnCl_2$ in the effluent entering the scrubber (solid, liquid, vapor, or combination of these). This variable would be determined by 1 and 2.
4. Retention time of the effluent at an elevated temperature. (Length of retention time at temperatures between the melting and boiling points of $ZnCl_2$ would probably determine particle growth, other variables being constant).

Plant waste heat might be utilized to obtain effluent conditions (exemplified by variables 1, 3, and 4) determined as optimum for maximum efficiency of $ZnCl_2$ removal.

VENTURI SCRUBBERS

Overcoming the corrosion problems experienced in attempts to control chloride-containing emissions with venturi scrubbers (noted in Chapter VIII) might be accomplished by two approaches to research and development.

Use of alkaline scrubbing solutions to neutralize the acidic corrosive effects of the chlorides being collected.

Alkaline compounds that might be tried in such scrubbing solutions include NH_4OH, $Ca(OH)_2$, NaOH and sodium phosphates. Also, investigators might try aqueous mixtures of insoluble alkaline-reacting substances, such as granulated limestone and the collected alkaline waste dust from portland cement processes (AEMPC, p.17). The success of this concept would depend on whether a solution composition and pH could be determined (the maintained) that would prevent corrosion but not cause precipitation of $Zn(OH)_2$ to an extent that would clog the gas-cleaning equipment.

Use of corrosion-resistant material.

Venturi scrubbing systems in which the venturi scrubbing unit and the cyclone separating unit (see Control Techniques, Fig. 4-18) are made of corrosion-resistant materials might be tried. Several conceptual material applications could be considered for this purpose.

1. Molded or laminated, fibrous glass reinforced, thermosetting plastics. Of the methods of fabricating the venturi and cyclone units with fibrous-glass-reinforced polyester, epoxy, or other thermosetting plastics, spray forming would probably be the least costly. Molding fiber-filled resin, mat laminating, and filament winding are further possibilities. Inserts made of corrosion-resistant metals or alloys, such as titanium, niobium, or other "reactive metals" might be used in the venturi throat and other areas of high gas velocity, if needed to resist abrasive wear and help dissipate heat (from friction and the sensible heat of the effluent). Aluminum and its alloys might also be tried as insert material (see Perry, p. 23-28). A further variation of this basic concept would be the use of thin shells or platings of corrosion-resistant metal over interior surfaces of the venturi and cyclone units. Also, metallic fibers might be incorporated in the plastic to conduct and dissipate heat.

2. Molded thermoplastics. Thermoplastics of some types might be molded to produce the units. A key consideration in selecting thermoplastics for this use would be the effluent temperature of the process to which the units would be applied. Findings of this study indicated that the usual temperatures of kettle-sweat process effluents are low enough to permit use of a wide range of thermoplastics, including some low-cost polyolefins; the higher temperatures of reverberatory-sweat process effluents would narrow that range (applicable to those processes), and could require usage of more expensive thermoplastics. Where conditions permit the use of polyolefins, the units could probably be used as "disposable" items, with frequent replacement, because of the low material cost. Rotational molding appears to be a promising method of fabricating the units. Supporting parts made of a low-cost metal might be used with the units to provide

rigidity and help dissipate heat. For example, the venturi and/or cyclone separator of a venturi system might be made of a molded plastic, and these parts might be enclosed in shells made of mild steel or aluminum, which could be opened to allow removal and replacement of the plastic parts when necessary. Carbon black incorporated in formulations might reinforce and otherwise enhance properties of plastics (particularly polyolefins) used in venturi scrubbing systems. Fibers of glass and/or metal might also be incorporated in the plastic for reinforcement and/or heat dissipation. Corrosion-resistant metallic inserts could be used in the venturi throat and other points of high gas velocity if needed to resist abrasive wear and to dissipate heat. Use of such inserts might be appropriate if a relatively expensive plastic were used.

3. Plastic-coated metal. The units might be made of low-cost metals such as mild steel or aluminum alloy, with coatings of rigid or elastomeric plastic that would withstand corrosion and abrasion. Coatings of polyurethane or vinyl plastisol might be tried for this purpose. The metal in such structures would provide rigidity and help dissipate heat.

4. Corrosion-resistant metals. The unit might be made entirely of corrosion-resistant metal. Metals that might be considered for this application include aluminum (see Perry p. 23-28), titanium, other reactive metals, and alloys of those metals. Mild steel coated with lead poses a further possibility.

BAG FILTERS

To overcome the problems incurred in bag filter application (noted in Chapters VIII-IX), two related determinations might be made. These are listed below, with concepts of bag filter development and application.

Determination of bag filter material

A determination would be made of bag filter materials having properties that show the most promise of resisting (1) the wetting, adhering, and corrosive effects of $ZnCl_2$ with adsorbed moisture from the effluent gas (mainly atmospheric moisture of infiltrated air), (2) frictional wear that occurs in cleaning fibrous-glass bag filters, and (3) elevated temperatures that might be maintained in effluent to minimize moisture adsorption.

Of currently availabel fibrous materials that might be considered for this determination, polyesters should be included. Also, fluorinated polymers should be investigated both as potential fiber materials and as coatings that might be applied to other fibers such as fibrous glass. Initial investigations of fluorinated material might include determining the availability or possible development of fibrous glass treated to obtain a fluorinated silicone coating on the glass fibers. Fluorinated-silicone-coated glass fibers might have the desired properties of resisting wetting, adhesion, corrosion, frictional wear (between fibers of woven threads), and high effluent temperatures.

Determination of limitations of $ZnCl_2$ particulate concentration for satisfactory bag filter collection

After determining the most promising bag filter materials, a determination should be made of the concentrations of $ZnCl_2$ in emitted particulate that limit use of bag filters (made of those materials) within the temperature range at which the effluent might be maintained. Higher temperatures would reduce the tendency of

$ZnCl_2$ to adsorb moisture. Therefore, one would expect correlation between effluent temperature and the maximum $ZnCl_2$ concentration in particulate that could be collected in a bag filter, higher $ZnCl_2$ concentration being tolerable at higher effluent temperatures. Effluent temperature is limited by the temperature resistance of the bag filter material. This determination might best be presented as a graph showing maximum $ZnCl_2$ concentration, as percent of emitted particulate, versus temperature of effluent entering the bag filter, bag filter materials being shown as parameters, and effluent moisture content (which would be determined mainly by ambient relative humidity) held constant at the maximum expected level. Other variables, including air-to-cloth ratio, and particulate emission rate, could also affect this correlation; thus several graphs might be required to represent a realistic range of process conditions. In this way, the useful range and the practicability of bag filters for controlling zinc sweat process emissions could be established.

Bag filters appear more promising for use with reverberatory-sweat furnaces than with kettle-sweat furnaces because of the following characteristics:

1. Combustion efficiency of reverberatory-sweat furnaces is higher, with consequent elimination of carbonaceous emissions where furnace design and operation are satisfactory. (Carbonaceous particulate could blind bags and pose a fire hazard in a baghouse.)

2. Effluent temperature of reverberatory-sweat furnaces is higher because of combustion products entering the effluent, which would reduce moisture adsorption by emitted $ZnCl_2$. This advantage might be offset in some instances by water vapor introduced by fuel combustion.

3. Dilution of emitted $ZnCl_2$ with ZnO particles is greater in reverberatory-furnaces, which generate more ZnO particles because of turbulence of air and combustion gas, and higher molten metal temperature.

ELECTROSTATIC PRECIPITATORS

To more fully establish the applicability of electrostatic precipitators and to optimize their usage for controlling zinc sweat process emissions, determinations might be made of the following:

1. Optimum materials, devices, and/or methods for overcoming corrosion of precipitator parts caused by chlorides collected in the precipitator (noted in Chapters VIII-IX).

2. The nature of any ignition hazards resulting from carbonaceous or other flammable emissions and limitations thereby imposed on use of electrostatic precipitators.

3. The ranges of particulate composition and other variables in which emissions control by means of electrostatic precipitators is satisfactory. This determination might be presented as graphs of collection efficiency versus $ZnCl_2$ concentration, with other variables such as effluent temperature, flow rate, and other chlorides present, held constant or shown as parameters.

AFTERBURNERS

Consideration might be given to developing a device and/or method for conserving afterburner fuel by stopping fuel combustion in afterburners when carbonaceous emission rates reach insignificant levels.

GRANULAR BED DEVICES

Granular bed devices may offer possibilities of controlling emissions containing $ZnCl_2$ because the moving granules of inert mineral would resist the corrosion and blinding that occurs with other filtering devices. (See GBD)

CONCEPTS OF UTILIZING COLLECTED PARTICULATE MATERIAL

In present emission control practice, emissions from zinc sweat processes that contain considerable chlorides are collected in two forms (1) aqueous mixtures from scrubbers containing $ZnCl_2$, ZnO, and sometimes small amounts of carbonaceous substances, and (2) mixtures of solid particles from electrostatic precipitators containing $ZnCl_2$ (with some adsorbed moisture), ZnO, and sometimes small amounts of carbonaceous substances. Developing uses for these materials would alleviate the problem of their disposal and allow more favorable economics of emission control systems. Four concepts of systems for utilizing these materials are presented and discussed.

CONVERSION OF COLLECTED PARTICULATE TO ZINC OXIDE AND ZINC CHLORIDE AS SEPARATE PRODUCTS

Collected particulate might be treated with steam in attempts to effect the reaction:

$$(1)\quad ZnCl_2 + 2\ HOH \rightarrow Zn(OH)_2\downarrow + 2HCl\uparrow$$

Since $Zn(OH)_2$ decomposes at 257°F, this reaction appears possible within the steam temperature range 212 to 257°F. Zinc hydroxide obtained from reaction (1) might be heated to produce ZnO at 257°F:

(2) $Zn(OH)_2 \xrightarrow{\Delta} ZnO + HOH\uparrow$

As an alternative approach, collected particulate might be treated with steam at temperatures of 257°F and higher to produce ZnO directly, through the reaction:

(3) $ZnCl_2 + HOH \rightarrow ZnO\downarrow + 2HCl\uparrow$

The HCl vapor formed in reaction (1) or (3) might be dissolved in water and the resulting acid reacted with additional, untreated, collected particulate to effect the reaction:

(4) $ZnO + 2HCl \rightarrow ZnCl_2 + HOH$

Settling, filtration, and/or evaporation might be applied to products to the above reactions to remove water.

Waste heat from secondary zinc processing furnaces and/or afterburners might be used as needed for this conceptual process, e.g. for the above-mentioned evaporation.

Thus, reactions (1), (2), and (3), by removing the chloride constituent from collected particulate mixtures, afford possible means of producing a mixture having high enough ZnO concentration and low enough chloride content to have commercial use. Reaction (4), by converting ZnO in collected particulate to $ZnCl_2$, might provide a highly concentrated $ZnCl_2$ mixture that could be recycled as flux.

REMOVAL OF CHLORIDE FROM COLLECTED PARTICULATE BY MEANS OF AMMONIA AND STEAM

Collected particulate might be treated with NH_3 and steam in attempts to effect the reaction:

(5) $ZnCl_2 + 2NH_3 + HOH \rightarrow 2NH_4Cl\uparrow + ZnO\downarrow$

The NH_3-steam mixture would have to be applied at a temperature higher than 212°F so that NH_4Cl could be separated as a vapor from ZnO. (See Figure 5-1 and Perry p. 3-44)

The objective of this concept is to produce a mixture having high enough ZnO concentration and low enough chloride content to be of commercial use. The NH_4Cl produced might be recycled as flux.

ZINC OXIDE ENRICHMENT OF COLLECTED PARTICULATE

Metallic zinc might be added to the material collected in scrubbers or precipitators to react the zinc with $ZnCl_2$ and water as follows:

(6) $ZnCl_2 + 2HOH \rightarrow Zn(OH)_2\downarrow + 2HCl$ (Solution)

(7) $2HCl + Zn \rightarrow H_2\uparrow + ZnCl_2$

One possible source of metallic zinc for this use would be the unmeltable attachments discharged from zinc sweat processes having residual crude zinc-alloy coatings.

These reactions indicate that as elemental zinc is added to a given quantity of collected particulates, the amount of $ZnCl_2$ in the mixture would remain constant but the amount of zinc present in the mixture as Zn $(OH)_2$ would increase.

The resulting mixture of collected particulate and products of the reactions would be heated to evaporate water and decompose $Zn(OH)_2$ to ZnO, at 257°F (Perry, p. 3-22). Plant waste heat might be used for this evaporation. Hydrogen from

Reaction (7) above might be utilized to produce heat or for other purposes (including a conceptual smelting system shown below). If the ZnO content of the collected particulate were enriched, the resulting material might be commercially acceptable.

SMELTING OF COLLECTED PARTICULATE USING HYDROGEN

In this concept, the material collected in electrostatic precipitators would be treated with H_2 at high temperature to effect the reactions:

(8) $H_2 + ZnCl_2 \xrightarrow{\Delta} 2HCl\uparrow + Zn\downarrow$

(9) $H_2 + ZnO \xrightarrow{\Delta} H_2O\uparrow + Zn\downarrow$

Free energy relationships should be investigated to determine whether these reactions appear promising.

CORRELATION OF CHARGED MATERIALS WITH EMISSION COMPOSITION

Relationships of charged materials with emission composition were shown in Chapter IX (page IX-5). Equations or graphs developed from those relationships would be useful for estimating the composition of emissions as percentages of $ZnCl_2$ and ZnO, or chlorine as Cl^- and total zinc, using data on amounts of $ZnCl_2$ flux and zinc charged to a sweat-process heat. Emission compositions estimated in this way might be used for further definition and refinement of process models and for selecting emission control systems, on theoretical bases, without the necessity of emission tests.

Developing these equations or graphs would depend on obtaining additional process and emission data. As additional data are obtained, perhaps incidental to subsequent development work, equations and graphs correlating charged materials with emission composition might be developed.

RECOMMENDATIONS FOR FURTHER RESEARCH AND DEVELOPMENT

The concepts developed here are based on indicated effects that are immediately apparent from characteristics of secondary zinc process emissions, brought out in this study. These concepts represent only a brief, initial treatment of those emission characteristics and indicated effects. Mainly, they reveal principles that can be utilized in developing emission control systems. Many variations and combinations of the concepts, and principals brought out by them might be used in the ultimate engineering of systems that will alleviate problems of controlling secondary zinc industrial emissions.

A more rigorous treatment of potential chemical reactions and physical occurrences, involving the emissions, than that shown here should be performed for the purpose of developing additional and/or alternative concepts that appear feasible.

Engineers and other specialists of NASMI, APCO, other concerned individuals and groups should be invited to recommend additional and/or alternative concepts.

The concepts, obtained as stated above, should be subjected to a screening study that would consist of theoretical and laboratory investigations, including consideration of technical and economic factors (the latter from Part 2 of this problem definition study; see Chapter I). Based on findings of that screening study, the most promising concepts should be selected and recommendations made for development and in-plant tests of prototype and/or demonstration emission control equipment.

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Appendix A

Derivation of Values for Process Models

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APPLIED FLUX

Processing with $ZnCl_2$ flux was assumed for all models. This condition seems reasonably representative as indicated by general findings of this study (see Table VI-2 and VI-3) and by the small amount of NH_4^+ indicated in analyses shown on page VI-5. Further, the fluxing action of $ZnCl_2$ and NH_4Cl are essentially the same, as shown in Chapter IV.

EMISSIONS FACTORS

Emission factors that were developed and presented in Chapter VI (page VI-4) were tabulated in column 7 of Table VII-1, page 1. Process conditions corresponding to those emission factors, as indicated by findings of Chapter VI, were tabulated in the preceding columns.

COMPOSITION OF CHARGES AND RATES OF APPLYING PROCESS MATERIALS

A residual scrap mixture, containing residual flux and no organic material, was assumed as making up the charge to Model A (Table VII-1, page 1, column 2).

Metallic scrap mixtures containing organic materials were assumed as making up part of the charges to Models B, C, D, and E (Table VII-1, page 1, column 2).

For Model A, the rates of charging scrap material and of applying flux were assumed as 1/4 ton/hour and 10 lb./hour respectively (Table VII-1, page 1, columns 4-5). These assumptions agree with the data shown for the first test tabulated in Table VI-2 and correspond with the emission factor 24.5.

Model B is similar to Model A except that metallic scrap containing organic material was assurmed as being included in the residual scrap charge. To arrive at a rate of applying flux to Model B, the rate for Model A was reduced from 10 to 8 to account for dilution of the flux content of the residual scrap charge by metallic scrap. The emission factor 24.5, assumed for Model A, was also assumed applicable to Model B because carbonaceous emissions resulting from organic material in the charge would tend to compensate (in quantity) for the reduction of chloride emissions due to the reduced amount of flux in the charge.

To establish the values representing process data for Model C (Table VII-1, page 1, columns 1-5), the process data shown for the fifth test tabulated in Table VI-2 were assumed. The published emission factor 10.8 (the last item tabulated in Table VI-2) was chosen for this model in preference to the emission factor 10.3, determined for the fifth test. This choice was made to be consistent with the literature and because the two emission factors are not significantly different, considering the general limited precision of emission tests and the approximation of process data noted in Table VI-2, column 4.

The mixture of the charge to Model D was assumed to be the same as that of Model B. The flux application rate for Model D (16 lb./hour was derived by increasing the rate shown for Model B (8 lb./hour) in proportion to the higher rate of charging scrap material to Model D.

For Model E, the rate of charging scrap material was assumed as 1 ton/hour. This value approximates the rate shown for the sixth item in Table VI-2. Process conditions of Model E (shown in Table VII-1) correspond to the emission factor 13, of the same sixth item. The rate of applying flux was assumed as 1 lb./hour to agree with the rate shown for processing similar scrap material in the second processing condition tabulated in Table VI-3.

PARTICULATE EMISSION RATES

Particulate emission rates for all models were calculated from the tabulated process weight rates and emission factors, as shown in Table VII-1, page 1, column 8.

COMPOSITION OF PARTICULATE EMISSIONS

A chemical analysis of particles emitted under process conditions similar to those of Model A was determined in Chapter VI and shown on page VI-9. This analysis was therefore tabulated for Model A in Table VII-1, page 1, columns 9-12.

The organic materials in the charges to Models B and C (kettle furnaces) were assumed to cause 10% carbonaceous content of particulate emissions (Table VII-1, column 12). This percentage was suggested by results of the particulate analysis shown on page VI-5.

The organic materials in the charges to Models D and E (reverberatory furnaces) were assumed to be completely incinerated. No emission data were obtained during this study to support this assumption. It is based on the experience of plant operators and on consideration of conditions in reberberatory furnaces that appear conducive to high combustion efficiency.

The amounts of $ZnCl_2$ and ZnO particulate emissions shown for Model B are based on those shown for Model A, but the percentage of $ZnCl_2$ in particulates is reduced to account for the reduced content of $ZnCl_2$ flux in the charge and for the added content of carbonaceous particles to emissions. The amounts of water of hydration and of deliquescence in emissions from Model B were estimated to accord with the $ZnCl_2$ content.

Since the scrap material charged to Model C and E is comprised of only metallic scrap and the amounts of flux applied are therefore small compared with the flux content of residual scrap, the amounts of emitted $ZnCl_2$ would also be relatively small. Particulate emissions of 5% and 4% $ZnCl_2$ were assumed representative of this condition for Models C and E respectively. These percentages correspond to an assumption that about half of the applied $ZnCl_2$ flux is emitted as particulates. The balance of the particulate emission constituents tabulated in Table VII-1 were calculated for these models to accord with the $ZnCl_2$ content, as shown in columns 9-12. The composition shown for particulate emissions of Model D (columns 9-12) is an approximation derived from the analysis of particulates emitted from a combination of one reverberatory and several kettle furnaces shown on page VI-8. The approximation was made by omitting the content of carbonaceous material from the analysis (of page VI-8) and recalculating percentages of $ZnCl_2$, ZnO etc. The percentages were weighted to increase the ratio of ZnO to $ZnCl_2$ because conditions in reverberatory furnaces indicate a tendency to higher ZnO emission rates, as compared with $ZnCl_2$. (See page VI-3.)

PARTICLE SIZE AND PARTICLE SIZE DISTRIBUTION

In tabulating particle size in Table VII-1, page 2, it was assumed that of the emitted $ZnCl_2$ and ZnO particles, those formed from vapor condensation and oxidation approximate 1-micron size, and that agglomerates of those particles reach sizes up to 10 micron. The balance of emitted particles would then consist mostly of entrained $ZnCl_2$ and ZnO particles, which would be larger, and of carbonaceous particles of various sizes. Distribution of the sizes of these particles was assumed as shown. These approximations appear reasonable in view of findings of Chapter VI. Not noted in this tabulation are the other chlorides and oxides, such as $AlCl_3$, that would be present in small amounts.

EFFLUENT GAS COMPOSITION

The effluent gas of Model A is considered as having the composition of dry air in accordance with findings of Chapter VI.

The effluent gas of Models B and C is also considered as having the composition of dry air except that 0.1% CO_2, 0.1% CO, and 0.1% H_2O content are assumed, to account for combustion of part of the organic material in the charge.

The range of effluent gas composition shown for Models D and E is the same as that shown for reverberatory sweat process emissions in Table VI-1. It is assumed that combustion of organic material in the charge is complete, and that the amount of that material is not large enough to significantly affect effluent gas composition.

EXHAUST EFFLUENT FLOW RATES AND TEMPERATURES

Effluent flow factors for all models shown in Table VII-1, page 2, column 6 were obtained from Table VI-1. Effluent flow rates shown in column 7 were calculated from those flow factors, as shown. Process bath temperatures shown in Column 8 were obtained from Table VI-2. Exhaust effluent temperatures shown in column 9 were obtained from pages VI-15 and 16.

Appendix B

Calculation of Amounts of Compounds Composing Particulate Emissions for Chapter VI

Calculation Sheet 1

Calculation Sheet 2

Calculation Sheet 3

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Appendix B

Calculation Sheet 1 - Calculation of Amounts of Compounds Composing Particulate Emissions for Chapter VI
Basis: 100 grams (each) of Samples 1 and 2

Atomic and Molecular Weights	Calculation of Amounts of Compounds in Basis Sample	
	Sample 1	Sample 2
NH_4^+ Atomic Wts.: N = 14; H = 1; Cl = 35.5 Molecular wt. of NH_4Cl: 14 + 4 + 35.5 = 53.5 Combined atomic wt. of NH_4 : 14 + 4 = 18	0.47 g NH_4 present in basis sample $\frac{NH_4^+}{NH_4Cl} = \frac{18}{53.5} = \frac{.47g}{\text{wt. of } NH_4Cl \text{ in 100g sample}}$ wt. of NH_4Cl in 100g sample = $\frac{.47g \times 53.5}{18}$ = 1.40g NH_4Cl	0.36g present in basis sample $\frac{18}{53.5} = \frac{.36g}{\text{wt. of } NH_4Cl \text{ in 100g sample}}$ wt. of NH_4Cl in 100g sample = $\frac{.36 \times 53.5}{18}$ = 1.1 g NH_4Cl
Cl- Atomic wt.: Cl = 35.5	8.93g Cl present in basis sample Amount of Cl in NH_4Cl in basis sample = 1.40 - .47 = .93g	8.32g Cl present in basis sample Amount of Cl- in NH_4Cl in basis sample = 1.07 - .36 = .71g
Zn Atomic wt.: Zn = 65.4 Molecular wt of $ZnCl_2$ = 65.4 + 2 X 35.5 = 65.4 + 70 = 135.4	47.5g Zn present in basis sample Amount of Cl in $ZnCl_2$ = 8.93g - .93g = 8.0g $\frac{2\ Cl}{ZnCl_2} = \frac{2 \times 35.5}{135.4} = \frac{\text{Amount of Cl in } ZnCl_2 \text{ in basis sample}}{\text{Amount of } ZnCl_2 \text{ in basis sample}}$ $= \frac{8.0g}{\text{Amount of } ZnCl_2 \text{ -}}$ Amount of $ZnCl_2$ in basis sample = $\frac{8.0g \times 135.4}{2 \times 35.5}$ = 15.3 g $ZnCl_2$	44.5g Zn present in basis sample Amount of Cl in $ZnCl_2$ = 8.32 - .71 = 7.61g $\frac{2Cl}{ZnCl_2} = \frac{2 \times 35.5}{135.4} = \frac{\text{Amount of Cl - - -}}{\text{Amount of } ZnCl_2 \text{ -}}$ $= \frac{7.61}{\text{Amount of } ZnCl_2 \text{ - -}}$ Amount of $ZnCl_2$ in basis sample = $\frac{7.61 \times 135.4}{2 \times 35.5}$ = 14.5g $ZnCl_2$
O Atomic wt.: O = 16 Molecular wt. of ZnO = 65.4 + 16 = 81.4	Amount of Zn in $ZnCl_2$ = 15.3 - 8 = 7.3g Amount of Zn in ZnO = 47.5 - 7.3 = 40.2g $\frac{Zn}{ZnO} = \frac{65.4}{81.4} = \frac{\text{Amount of Zn in ZnO in basis sample}}{\text{Amount of ZnO in basis sample}}$ $= \frac{40.2g}{\text{Amount of ZnO in basis sample}}$ Amount of ZnO in basis sample = 40.2g X $\frac{81.4}{65.4}$ = 50.0g ZnO	Amount of Zn in $ZnCl_2$ = 14.5 - 7.6 = 6.9g Amount of Zn in ZnO = 44.5 - 6.9 = 37.6g $\frac{Zn}{ZnO} = \frac{65.4}{81.4} = \frac{\text{Amount of Zn in ZnO in basis sample}}{\text{Amount of ZnO in basis sample}}$ $= \frac{37.6g}{\text{Amount of ZnO -}}$ Amount of ZnO in basis sample = 37.6g X $\frac{81.4}{65.4}$ = 46.9g

Appendix B

Calculation Sheet 2 - Calculation of Amounts of Compounds Composing Particulate Emissions for Chapter VI

Basis: 100 grams (each) of Samples 1 and 2

Atomic and Molecular Weights	Calculation of Amounts of Compounds in Basis Sample	
	Sample 1	Sample 2
Al Atomic wt.: Al = 27.0 Molecular wt. of Al_2O_3 = 2 X 27.0 + 3 X 16.0 = 54.0 + 48.0 = 102.0	1.43 g Al present in basis sample $\frac{2\ Al}{Al_2O_3} = \frac{2 \times 27.0}{102} = \frac{1.43g}{\text{Amount of } Al_2O_3 \text{ in basis sample}}$ Amount of Al_2O_3 in basis sample = $1.43g \times \frac{102}{2 \times 27}$ = 2.7g Al_2O_3	0.54 g Al present in basis sample $\frac{2Al}{Al_2O_3} = \frac{2 \times 27}{102} = \frac{0.54g}{\text{Amount of } Al_2O_3 \text{ in basis sample}}$ Amount of Al_2O_3 in basis sample = $.54g \times \frac{102}{2 \times 27}$ = 1.02 g Al_2O_3
Fe Atomic wt.: Fe = 55.8 Molecular wt. of Fe_2O_3 = 2 X 55.8 + 3 X 16.0 = 111.6 + 48.0 = 159.6	0.40gFe present in basis sample $\frac{2\ Fe}{Fe_2O_3} = \frac{2 \times 55.8}{159.6} = \frac{.40g}{\text{Amount of } Fe_2O_3 \text{ in basis sample}}$ Amount of Fe_2O_3 in basis sample = $.40g \times \frac{159.6}{2 \times 55.8}$ = 0.57 g Fe_2O_3	0.21g Fe present in basis sample $\frac{2\ Fe}{Fe_2O_3} = \frac{2 \times 55.8}{159.6} = \frac{.21g}{\text{Amount of } Fe_2O_3 \text{ in basis sample}}$ Amount of Fe_2O_3 in basis sample = $.21g \times \frac{159.6}{2 \times 55.8}$ = 0.30 g Fe_2O_3
Pb Atomic wt.: Pb = 207.2 Molecular wt. of PbO = 207.2 + 16 = 223	0.14g Pb present in basis sample $\frac{Pb}{PbO} = \frac{207}{223} = \frac{.14g}{\text{Amount of PbO in basis sample}}$ Amount of PbO in basis sample = $.14g \times \frac{223}{207}$ = 0.15g PbO	0.16 g Pb present in basis sample $\frac{Pb}{PbO} = \frac{207}{223} = \frac{.16g}{\text{Amount of PbO in basis sample}}$ Amount of PbO in basis sample = $.16g \times \frac{223}{207}$ = 0.17g PbO
H_2O - Water of hydration in $ZnCl_2 \cdot 4H_2O$ Molecular wt. of H_2O = 2 + 16 = 18 1 mol H_2O = 18g H_2O 1 mol $ZnCl_2$ = 135.4g $ZnCl_2$	mols $ZnCl_2$ in basis sample $= 15.3\ \cancel{g\ ZnCl_2} \times \frac{1\ mol\ ZnCl_2}{135.4\ \cancel{g\ ZnCl_2}} = \frac{15.3}{135.4}\ mol\ ZnCl_2$ For every mol of $ZnCl_2$ in basis sample, there would be 4 mols of H_2O. H_2O (water of hydration) $= \frac{15.3\ \cancel{mol\ ZnCl_2}}{135.4} \times \frac{4\ \cancel{mol\ H_2O}}{\cancel{mol\ ZnCl_2}} \times \frac{18g\ H_2O}{\cancel{mol\ H_2O}}$ = 8.1 g H_2O	mols $ZnCl_2$ in basis sample $= 14.5\ \cancel{g\ ZnCl_2} \times \frac{1\ mol\ ZnCl_2}{135.4\ \cancel{g\ ZnCl_2}} = \frac{14.5}{135.4}\ mol\ ZnCl_2$ H_2O (water of hydration) $= \frac{14.5}{135.4} \times 4 \times 18$ =7.7 g H_2O

Appendix B

Calculation Sheet 3 - Calculation of Amounts of Compounds Composing Particulate Emissions for Chapter VI - Basis 100g of sample

17.7g Cl present in basis sample
48.5g Zn present in basis sample

$$\frac{2\ \mathrm{Cl}}{\mathrm{ZnCl_2}} = \frac{2 \times 35.5}{135.4} = \frac{\text{Amount of Cl in } \mathrm{ZnCl_2} \text{ in basis sample}}{\text{Amount of } \mathrm{ZnCl_2} \text{ in basis sample}}$$

$$= \frac{17.7\mathrm{g}}{\text{Amount of } \mathrm{ZnCl_2} \text{ in basis sample}}$$

Amount of $ZnCl_2$ in basis sample = $17.7\mathrm{g} \times \frac{135.4}{2 \times 35.5} = \frac{17.7 \times 135.4}{71}$

= $\underline{33.8\mathrm{g}\ \mathrm{ZnCl_2}}$

Amount of Zn in $ZnCl_2$ = 33.8 - 17.7 = 16.1g (in basis sample)

Amount of Zn in ZnO = 48.3 - 16.1 = 32.1g (in basis sample)

Amount of ZnO in basis sample = $32.1\mathrm{g} \times \frac{81.4}{65.4} = \underline{40.0\mathrm{g}\ \mathrm{ZnO}}$

H_2O (water of hydration) = $\frac{33.8}{135.4} \times 4 \times 18\mathrm{g}\ \mathrm{H_2O} = \underline{18\mathrm{g}\ \mathrm{H_2O}}$

Secondary Zinc and Aluminum Industries, Emission Control Problem Definition Study

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(page 1 of 2)

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CEP, 3/67	*Chemical Engineering Progress*, March '67, "Removing Solid and Mist Particles" by Morash, Krouse, and Vosseller, pp 70-74.
AE, Nov. 1967	*Air Engineering*, Nov. '67, "Zinc Oxide Emissions at Baltimore Smelter Controlled by Dust Collection System", pp 18-20
Perry	*Perry's Chemical Engineers' Handbook*, ed. Perry, Chilton and Kirkpatrick, Fourth Edition (McGraw-Hill) 1963.
Donoso	*NASMI's First Air Pollution Control Workshop*, 1967, "Utilization of Scrubbers and Precipitators" by J. Donoso.
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GBD	*Evaluation of Granular Bed Devices*, Final Report, Contract No. PH 86-67-51, Phase III, AVATD-0107-69-RR, June 1969, Avco Division, Lowell, Mass. (NAPCA).
AEMPC	*Atmospheric Emissions from the Manufacture of Portland Cement* by Kreichelt, Kemnitz and Cuffe (PHS) No. 999-AP-17, 1967.

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ERRATA FOR SECONDARY ZINC INDUSTRY EMISSION CONTROL PROBLEM DEFINITION STUDY, PART 1 - TECHNICAL STUDY FINAL REPORT

Title Page - Insert the date "May, 1971" after the statement "Conducted by the AIR POLLUTION CONTROL OFFICE, EPA, in cooperation with THE NATIONAL ASSOCIATION OF SECONDARY MATERIAL INDUSTRIES".

Page (V-4) - At the bottom of this page, begin new paragraph by inserting the following line:

"Findings of this study indicate that there are significant carbonaceous"

Table VII-1 (Page 1 of 2) - In Column 7, the fourth item from the top, delete the decimal point that precedes the number "32".

Page (VIII-14), second line - Delete "thorough" and substitute "through".

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